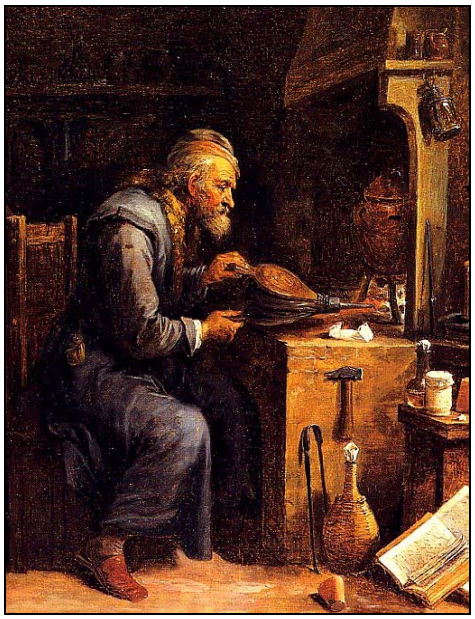
ASSAYING AND SMELTING NOBLE METALS IN SIXTEENTH-CENTURY AUSTRIA: A COMPARATIVE ANALYTICAL STUDY



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Abstract

This thesis aims primarily at furthering our understanding of the technologies involved in the metallurgy of precious metals during the Renaissance, by combining a critical evaluation of historical texts with the analytical study of contemporary archaeological remains. In particular, this work focuses on high-temperature processes performed in the fire assay and smelting of ores, by investigating two archaeological case studies from sixteenth-century Austria: the small-scale laboratory of Oberstockstall – the most complete Renaissance laboratory ever recovered –, and the contemporary large-scale gold smelting site of the Angertal. The analytical techniques used are optical microscopy, X-ray fluorescence, and scanning electron microscopy-energy and wavelength dispersive spectrometry.

In the Oberstockstall laboratory, the study of high-temperature residues produced in triangular crucibles, scorifiers and cupels allows a detailed examination of fire assay practice. The main technical sequence identified is a three-step fusion-scorification-cupellation process, performed on fahlores for their precious metal content, together with a wider range of experimental chymical activities, testing the properties of new materials and illustrating approaches that would prove fundamental in the development of chemistry and modern science.

The analyses of metallurgical remains from the contemporary gold smelting site in the Angertal indicate that silver and gold were extracted from a variety of sulphidic minerals characteristic of the regional mineralisation, employing a very standardised technological sequence. Smelting such ores created lead bullion at the bottom of the furnace, which collected most of the noble metals, fayalitic slag on top, and matte in between. The significant gold and silver losses in matte, documented through experimental cupellation of archaeological samples, suggest the possibility of matte being re-smelted, while it demonstrates in practice the links that would have existed between small- and large-scale metallurgical processes.

The archaeological and historical contextualisation of these reconstructions, and comparison with contemporary technical treatises, allow a detailed insight into early modern gold and silver extraction and highlight the potential of future work.

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Chapter 1 – General introduction

> "Because gold is a compound mineral praised by philosophers and all wise men as being of the highest perfection among all mixed minerals, and because of its great beauty, it is the universal opinion that it possesses extraordinary powers that are beneficial to men".
>
> (Biringuccio 1540, *De La Pirotechnia* – translated by Smith and Gnudi 1991, p. 26)

This thesis presents the combined archaeometric and historical study undertaken on the technologies employed in the metallurgy of precious metals in early modern Europe. The above statement borrowed from Biringuccio could explain in a few words the reasons behind the research carried out for this PhD project: the wide fascination of humanity for gold, as one of the generally most valued materials in both economic and aesthetic senses. This justification would, however, be too simplistic a view, and this thesis indeed stems not only from this general interest in the metal itself, but also, as shown below, from the need to increase our incomplete knowledge of the pre-modern metallurgy of noble metals. This initial chapter explains the research questions to be addressed within this project, and discusses in more detail the real *raison d'être* of this project. An outline of the structure of this thesis concludes this chapter.

1.1. Research aims and objectives

The first key aim of this research was to understand Renaissance metallurgical and chemical technologies and processes performed on gold- and silver-bearing ores to extract these noble metals, on both a large industrial scale and a small laboratory scale. For this purpose, this project is based on two case studies from sixteenth-century Austria. The first site is a small-scale Renaissance laboratory located in the castle of Oberstockstall, in Lower Austria, and related to chymical[1] and metallurgical activities with strong connections to precious metals. The second one is an industrial gold smelting site situated in the Angertal, in the Gastein region, and

[1] The terms 'chymistry', 'chymist'and 'chymical' and the reasons for their utilisation in the context of Oberstockstall are fully explained in chapter 2.

for which the peak of production is thought to have been contemporary to the lifespan of the Oberstockstall laboratory. For both archaeological sites, various issues have been raised and addressed. The first set of questions has concerned the characterisation and analysis of the archaeological materials related to the various high-temperature processes. These are predominantly metallurgical waste, such as slag and matte, and ores and lead metal. The interpretation of thescientific study of these archaeological remains has enabled the high-resolution reconstruction of sequences of metallurgical operations, and the identification of working parameters and potential fluxes and additives mixed in the charge.

The specific issues related to the metallurgical technologies identified have been more broadly contextualised within their wider historical and cultural contexts. For the Angertal gold smelting site, it was important to incorporate historical accounts and the study of archaeological samples from nearby contemporary mines to try to understand the role this smelting site may have played in this widely exploited region, and correlate both types of evidence – historical and archaeological –, when attempting to understand the organisation of the ore supply from the local mines and whether there was a specific mine taking on the role of supplier for the Angertal area, the scale of production this site covered, and where and in which form the metal was traded to. On the other hand, in addition to comprehensively document the Renaissance practice of small-scale fire assaying, the special status of the laboratory of the Oberstockstall Castle – owned and probably used by priests during the period studied – provides a unique opportunity to investigate the level of awareness and understanding of nature, especially at a time when the concept of science and the perception of the material world were radically different from ours.

The second major aim of this project was to juxtapose the recommended processes described in major Renaissance technical treatises with the actual sixteenth-century practice identified through the analysis of archaeological material. This has been achieved through the critical review and interpretation of written recipes from the relevant metallurgical texts, in terms of modern chemical and metallurgical understanding. The comparison between these recipes and the actual processes identified has shown the similarities and differences existing between historical sources and contemporary practice.

The initial questions of this research have subsequently led to a wider interpretation regarding the influence of the then newly-written texts on metallurgy in the sixteenth century on practitioners, being metallurgists, chymists, or any other craftsmen or scholars, who would have needed to consult them, and also the meaning of these recipes in terms of human perception of matter. In other words, Renaissance metallurgists and chymists might have performed similar operations to nowadays but with a different view of the materials and chemical reagents they were using and of the reactions they were witnessing. The Renaissance was a very important period of change in the philosophy and understanding of nature. Old theories of matter were starting to be rejected as new ones were developed, and it is hoped that this work has contributed to illustrate what is probably the origins of our modern perception of matter.

Gold and silver are both geologically and culturally related, and their metallurgies therefore should be studied together. Likewise, the small- and large-scale counterparts are seen as two sides of the same coin. This is why the results obtained from these two sites have been compared in order to explore the Renaissance metallurgy of gold and silver in its full range. Both sites have also been contrasted to relevant academic studies, so as to get a broader view of the metallurgical practice of precious metals in the sixteenth century.

Overall this research intends to offer a new insight into practical aspects of the history of science and technology, as well as hoping to make a relevant contribution to the combination and comparison of historical, archaeological and analytical sources.

1.2. The need for further research in the metallurgy of noble metals and the importance of this project

Our knowledge of the pre-modern primary metallurgy of gold and silver is still far from being comprehensive and clearly needs further research. The scope of this thesis is to develop and broaden our understanding of techniques and technologies applied during the extractive metallurgy of the precious metals in specific contexts. The two contemporaneous case studies selected for this research project are particularly appropriate to address this issue as they allow the characterisation of unique archaeological material that has not been studied before, the contextual

determination of specialised operations as performed in Renaissance metallurgy, and the comparison between small and large scales, at a time of great philosophical changes.

One part of this study is the continuation of an ongoing project which started with the archaeological, historical and archaeometric characterisation of the technical and domestic ceramics, glassware and some metallic artefacts from the laboratory of Oberstockstall (Soukup and Von Osten 1991; 1992; Von Osten 1992; Soukup *et al.* 1993; Soukup and Mayer 1997; Von Osten 1998; Rehren 1998; Martinón-Torres *et al.* 2003; Martinón-Torres 2005; Martinón-Torres and Rehren 2005a; Martinón-Torres and Rehren 2005b; Martinón-Torres and Rehren 2009). These initial investigations have given very promising results towards the understanding of this case study and the explanation of wider issues related to the development of chemistry and modern science in the sixteenth century. However, a large gap remained in the study of this assemblage, as no study had previously focused on the residues within the instruments as direct evidence for the activities carried out in the laboratory. This project was therefore carried on by focusing on the utilisation of the technical ceramics through the characterisation of metallurgical remains produced by high-temperature processes, such as bullion, matte and slag, in the form of residues within these reaction vessels as well as separate debris. The matte cakes have been of special interest, as they proved to be a very informative archaeometallurgical residue, which has rarely been studied before, except for one study by Rehren *et al.* (1999) on medieval smelting of lead-silver ores. Though not thoroughly studied, this type of material has been acknowledged in several studies of early European metallurgy (for instance Keesman 1993; Bachmann 1993; Goldenberg 1996). On the whole, the research on this laboratory has attempted to provide a systematic reference study of the most comprehensive Renaissance fire assay remains ever recovered.

The second case study selected for this research is a major Austrian industrial gold smelting site located in the Gastein Valley close to the numerous well-known gold mines situated in the mountains of the Hohe Tauern. The special location of this smelting plant in the heart of a widely recognised mining region, where the main activity took place from the medieval period onwards, and the variety, quality and quantity of archaeological material recovered, such as slag and matte fragments, furnace remains, or pieces of ore made it an ideal case study for the purpose of this

research. For this site as well, a more specific discussion has been dedicated to matte, as it has never been properly studied before and proved crucial in the understanding of the high-temperature reaction. The characterisation of this site has allowed the full reconstruction of an industrial gold smelting process in the Renaissance – probably the first to this extent for this region and period –, and, more generally, an improved appreciation of large-scale metallurgical technologies in central Europe at that time.

These two unique contemporary sites, which are of radically different scale and context, could seem unrelated at first glance, except for their connection to metallurgy and precious metals. However, at the mining sites in the neighbourhood of the Angertal valley, fire assay would have most likely been a routine operation performed on samples of ore before deciding to mine and smelt (or not) in great quantity. Fire assay was indeed carried out at the contemporaneous Frobisher's prospecting site in Canada (Unglik 2000; Beaudoin and Auger 2004) and is also historically documented by Ercker at the mines of Kutnà Hora (Kuttenberg) (Sisco and Smith 1951: 43). There is further evidence for the assaying of ores in the Black Forest in the early modern period (Goldenberg 1993: 237; Goldenberg 1996: 116-122; Schifer 1998; Rehren 2002). On the other hand, the Oberstockstall laboratory, being so rich in various instruments and vessels, could have either been a chymical or metallurgical laboratory, or most probably both. In this laboratory, small-scale fire assay may have been carried out for prospectors wishing to know the quantitative content of their ores in precious metals. The case of fire assay performed for mining people is well illustrated by Count Wolfgang II von Hohenlohe (1546-1610), a chymist carrying out metallurgical operations such as the assaying of ores with that particular purpose (Weyer 1992). However, the chymist(s) in Oberstockstall may have performed a more qualitative testing of these minerals containing precious metals with wider research purposes in mind. They may have been studying the properties of materials such as metals, metalloids such as antimony or bismuth, and matte, in order to increase their knowledge and understanding of nature. In addition to contributing to the history of technology by reconstructing practical processes not documented before, this research provides information on wider historical issues, such as the emergence of modern science through experimentation.

The comparison between historical sources and archaeometric data has brought new insight in the relationships existing between written procedures and practical

operations. Agricola (1556) states in his *De Re Metallica*, that "[t]he method of assaying ore used by mining people, differs from smelting only by the small amount of material used" (Hoover and Hoover 1950: 220). Similarly, Biringuccio explains that "the assay of all metal ores is made by means of fusion and they are brought to their fineness in the same way as if they were a large quantity" (Smith and Gnudi 1990: 136). There are several texts describing smelting and assaying techniques since Antiquity (Bailey 1929; 1932; Gunther 1959; Osbaldeston and Wood 2000), and a few accounts during the medieval period by Theophilus, who describes small-scale cupellation as well as copper smelting (Hawthorne and Smith 1979: 96-97, 139-140). Several texts on assaying emerge at the beginning of the sixteenth century in the *Probierbüchlein* (*ca.* 1520; Sisco and Smith 1949) and in *De la Pirotechnia* (Biringuccio 1540; Smith and Gnudi 1990); Agricola with his *De Re Metallica* (1556; Hoover and Hoover 1950) and Ercker with his *Treatise on Ores and Assaying* (1580; Sisco and Smith 1951) remain the main contributors to precise and reliable written explanations on smelting and assaying. However, Agricola's statement comparing small and large scales would need to be verified in practice, as he does not give the reader any particular justification for this argument, such as his observing this phenomenon. This question has not been investigated before, except for an introductory discussion of the subject by Rehren (2003), and this study therefore aimed at addressing this issue by contrasting the practice of the small- and large-scale metallurgies of noble metals, respectively assaying and smelting. This comparison between the archaeological and scientific data from both sites and documentary sources has been applied more generally and systematically to the most relevant high-temperature processes related to the extractive metallurgy of gold and silver.

1.3. Structure of the thesis

This general introduction presenting the overall research purpose is followed by chapter 2, which explains the background to the whole project. First, a a brief outline of the history of the metallurgy of the precious metals is presented, with a particular focus on fire assay, as one of the main high-temperature procedures, which would play an essential role in the development of modern science. This chapter then introduces the two case studies of Oberstockstall and the Angertal, detailing their

historical and archaeological contexts, excavated assemblages and previous studies carried out on them. Special attention is given at the end of this chapter to the theoretical framework in which this study is placed, by presenting relevant theoretical approaches to the study of ancient technologies and technical materials. This overall wider framework of this thesis has been borrowed from a previous PhD research carried out on technical ceramics, and especially on crucibles, which allows for archaeometric studies of archaeological artefacts to be specifically contextualised (Martinón-Torres 2005).

This thesis pursues with the description of the methodology selected for this project (chapter 3), which was deemed appropriate to address the research questions defined earlier and allows for comparison with other relevant studies. The principles and operating parameters of the various analytical techniques used are briefly explained, and the reasons for the choice of the particular combination of instruments and overall methodology are given. In addition, issues such as the selection of samples, the sub-sampling of the archaeological assemblage and the invasive sampling of selected artefacts and debris are justified.

Chapter 4 is dedicated to the extensive presentation of the various recipes and metallurgical procedures performed in the small- and large-scale productions of precious metals, as they are described in historical sources from the sixteenth century, with the main focus on high-temperature procedures, namely fire assaying and smelting. The main written sources considered in this study are the three metallurgical texts by Agricola, Ercker and Biringuccio. References to additional relevant written accounts are made whenever necessary while discussing and interpreting the results of the present study.

The study of the Oberstockstall material and the interpretation of the scientific results are the core of chapter 5. This chapter is divided into three main parts, each discussing a particular type of metallurgical waste product, namely crucible residues, bullion and matte cakes, and scorifiers residues – with a short fourth section on cupel remains that has also been included to complement the technical sequence identified, summarising previous published studies. The various technical and metallurgical remains are extensively described both macroscopically and microscopically, and the results of their analytical characterisation thoroughly presented and interpreted, as such remains have virtually never before been studied to this extent. This chapter therefore introduces the first systematic study of matte and fire assay remains as well

as the identification of small-scale practical methods and procedures to assay ores for their content in precious metals.

This chapter on the small-scale laboratory of Oberstockstall is followed by the results of the archaeometric study on the archaeological material from its large-scale counterpart, namely the gold smelting site of the Angertal. Chapter 6 is organised in a similar manner to chapter 5 in terms of the presentation of the remains and interpretation of the data, to allow for an easier comparison later on. This chapter starts with the macroscopic description of the various finds divided by type of material – i.e. ore, slag, matte, furnace wall and metal –, also including relevant samples from the nearby mining sites of the Bockhart and the Erzwies. This follows with the presentation of the microscopic and analytical data, and ends with the discussion of the scientific characterisation of this case study, which has led to the reconstruction of the smelting process carried out at this site in the sixteenth century. A specific section of this chapter has been devoted to the experimental cupellation of archaeological samples of lead and matte from the Angertal, and presents the results of this experiment as well as of the analysis of the gold-silver beads produced, the used cupels and, in the case of the matte fragments, of an iron-rich by-product. This particular experiment, while providing useful data for the recontsruction of the Angertal metallurgical technology, is also of relevance as it links the laboratory of Oberstockstall, where cupellation has been documented archaeologically, to the smelting region of the Angertal, where no direct archaeological evidence has been found but for which fire assay and cupellation might have been a routine operation at the local mining sites.

In the light of the data presented in chapters 5 and 6, chapter 7 contrasts the results of the two case studies, while considering additional publications of similar sites and/or materials when relevant. This chapter discusses wider implications inferred by the results of more specific issues, these broader research questions having been examined within the specific historical and cultural contexts of each site. They include the investigation of the status of the laboratory of Oberstockstall, which can potentially reflect both routine fire assay and experimentation more generally linked to research and development, and the levels of standardisation and optimisation of the smelting procedure of the Angertal, and the overall organisation of the plant. Technical sequences identified at both sites are then discussed in contrast with their contemporary descriptions from historical sources. This chapter

concludes with the comparison of both procedures in order to establish differences and similarities between the two sites and attempt to explain the reasons behind the variations observed. At this stage, it will have hopefully been shown that this research has contributed to our knowledge of the pre-modern metallurgy of the precious metals as initially intended. This project has also attempted to establish a systematic study of archaeological artefacts and remains rarely studied before, and to reiterate the importance of the need for contextual studies. Chapter 8 presents the main conclusions of this research project and outlines potential routes for future work.

The appendices include the full tables of bulk chemical compositions of the Angertal samples by ED-XRF, and of the standards and reference materials used to test the precision and accuracy of this instrument. They also contain the chemical compositions of the main phases of the samples from Oberstockstall, analysed by SEM-EDS and only given as averages within the thesis.

Chapter 2 – Project background

This research project intends to shed light on the sixteenth-century practice of metallurgical operations related to precious metals, both on the laboratory scale and as industrial production, and to compare these practical procedures, as identified through the archaeometric study of archaeological material, to processes as they are explained in contemporary texts. This chapter introduces the historical context of this research, by succinctly describing the beginning and progress of the metallurgy of precious metals until the early modern period, assessing the importance of fire assay in this metallurgy. It is also introducing the sixteenth-century written sources most relevant to this study, which will be fully presented in a later chapter (cf. chapter 4). For each of the two archaeological sites of Oberstockstall and the Angertal, a brief historical overview is followed by a presentation of their archaeological context, and a short introduction to the type of materials excavated and selected for this study. The latter will be more thoroughly addressed in chapters dedicated to their study (cf. chapters 5 and 6). This section will also introduce the theoretical framework in which this research is placed.

2.1. Historical context

2.1.1. The metallurgy of precious metals: inception and development until the sixteenth century

Precious metals have always been of interest to humans, be it for their appearance, their properties or their symbolic and economic value. Gold occurs predominantly as a native metal, often found in alluvial deposits and river sand but also in veins, where it usually occurs in minute amounts interspersed in other minerals, such as quartz or pyrite. This metal does not necessarily require a complex technology to be extracted from its alluvial deposits, indeed it was among the first ones to be exploited worldwide (Eluère 1983; Craddock 1995: 144-148). The earliest gold artefacts known were discovered in the cemetery of Varna, Bulgaria, dated to the fifth millennium BC (Eluère 1989; Morteani and Northover 1995; Gale *et al.* 2003). Some of the earliest mines known, which also date to the Late Neolithic-

Chalcolithic period and were associated with the exploitation of copper ores, were found in eastern Europe at Rudna Glava, Serbia (Jovanovic 1980; 1982; Craddock 1995: 58-60) and Ai Bunar, Bulgaria (Cernych 1978), and at the slightly later Near Eastern sites of Timna, Israel (Rothenberg 1972; Conrad and Rothenberg Conrad and Rothenberg 1980; Craddock 1995: 64-69) and Feinan, Jordan (Hauptmann 1989; Hauptmann *et al.* 1992; Craddock 1995: 66, 127). The inception of smelting took place in Europe during this same fifth millennium, with evidence of early copper smelting in south Spain and the Alps (Montero Ruiz 1993; Höppner *et al.* 2005), and was an essential step forward in the history of metallurgy. It also contemporaneously developed in south-west Asia, with extensive evidence found at Timna and Feinan (Rothenberg 1972; Hauptmann 1989; Hauptmann *et al.* 1992). Mining skills and methods kept improving from the fifth and fourth millennia BC onwards, with various technological breakthroughs and innovations, such as the introduction of fire setting (Craddock 1992), metal tools – subsequently replacing stone tools such as stone hammers –, ventilation and drainage systems to allow mining at greater depths (Craddock 1995: 47-48, 63-64, 71-81).

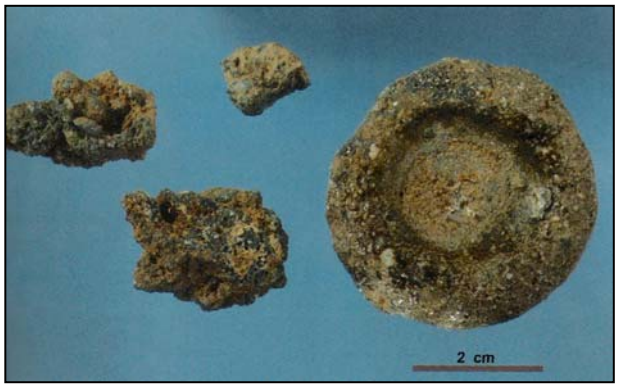
There is early evidence for the recovery of native gold from sands in the Nubian desert, dated to at least the fourth millennium BC (Forbes 1954: 580). There is plenty of evidence for the early production and use of gold in Europe; however, the extensive exploitation of its primary ores was not a straight and fast process and was established only over a relatively long period of time. Silver was not exploited as early as gold and the reason for its later exploitation is different. Although it also exists as a native metal – but with an exploitable proportion most probably more limited in ancient times compared to copper and gold (Patterson 1971: 299) – and there is evidence of the early use of silver in its native form, for instance in the Aegean in the Bronze Age (Renfrew 1967), silver mainly occurs in compound form in veins and is often associated with lead, sulphur and other base metals. It was therefore necessary to wait for cupellation to be discovered during the fourth millennium BC (Nriagu 1985) to be able to separate the silver from base metals, especially lead. The earliest cupellation process known in the context of primary silver production was performed at the late fourth millennium BC site of Habuba Kabira in Syria (Kohlmeyer 1994; Pernicka *et al.* 1998) and a small scale two-step process including cupellation has been identified at the contemporary site of Fatmali-Kalecik in East Anatolia (Hess *et al.* 1998). There is also evidence of lead-silver ore

extraction and of cupellation at various Early Bronze Age sites in Siphnos, with potential mines related to the exploitation of gold (Wagner *et al.* 1980). In addition, recent excavations have unveiled a large quantity of cupellation remains at the site of Lambrika in south-eastern Attica, dated to the final Neolithic-Early Bronze Age period (Georgakopoulou *et al.* 2008; Georgakopoulou, *pers. comm.*). There are, in comparison, only rare early silver finds from the same period discovered in the Levant (Prag 1978; 1986; Philip and Rehren 1996), a region where significant metallurgical knowledge existed at that time. One major issue in the ancient metallurgy of silver is the high probability that the quantity of excavated material only represents a small fraction of the actual amount of silver produced and traded in ancient times (Philip and Rehren 1996) due to extensive recycling.

Smelting techniques spread and developed gradually across Europe through the Bronze Age and the Iron Age, mostly in the context of copper production, changing from a relatively basic non-slagging process – at least no evidence of slag has so far been found – to the then widely known slagging process (Craddock 1995: 144-148), and overall increasing the scale of metal production. This, probably combined to the exhaustion of oxidic ores (Patterson 1971: 311), and the developments of mining techniques, led to the exploitation of a wider range of ore minerals, such as sulphides, from the Early Bronze Age onwards in various parts of the world (Hauptmann *et al.* 2003; Ixer and Pattrick 2003), although it seems that in specific regions such as the Balkans, these minerals were possibly already smelted in the fifth millennium BC alongside oxides (Ryndina *et al.* 1999; Gale *et al.* 2003). Many of the present day sulphide deposits may however have been mostly oxides in Antiquity, making it difficult in most cases to identify the nature of the ore deposits in ancient times (Craddock 1995: 10-11).

Late Bronze Age slag from the smelting of complex ore for its silver content has been found in south-west Spain (Rothenberg and Blanco-Freijeiro 1981; Kassianidou 2003), and argentiferous lead ores, mostly galena, were smelted on a large scale at Laurion during the Classical period, as evidenced by the vast beneficiation complex (Conophagos 1980; Tylecote 1987: 125, 135; Rehren *et al.* 2002; Rehren 2005). Contemporaneously, during the first millennium BC, gold was extensively recovered from placers (alluvial deposits) and mined from veins in the Celtic world (Northover 1995), a good example being the Celtic gold mines in the region of the Limousin, France (Cauuet 2004) (Fig. 2.1). This period was also the time of the Lydian

civilisation and their King Croesus, famous for his colossal wealth gained from the exploitation of alluvial gold, which was refined to produce the first coinage ever known (Ramage and Craddock 2000) (Fig. 2.2).



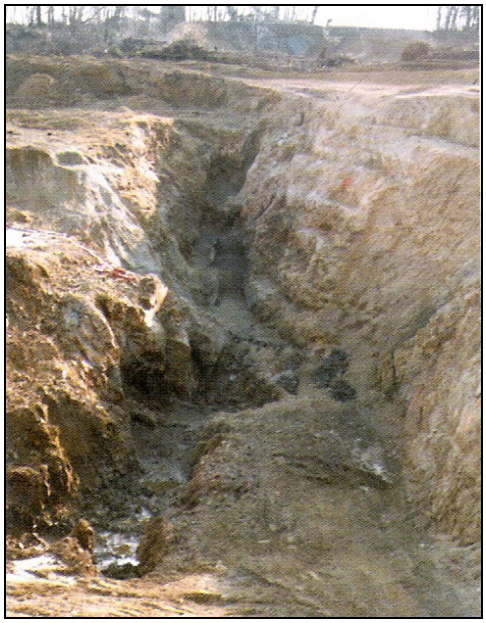


Fig. 2.1. *Fourth-third century BC crucibles from Cros-Gallet Nord, France (above) and excavation of a La Tène gold mine at la Fagassière, France (right) (after Cauuet 2004: 43, 77).*

Fig. 2.2. *Lydian Croeseids from Sardis,Turkey made of pure gold: two of the earliest coins known (after Ramage and Craddock 2000: 129).*

In the particular context of the metallurgy of gold and silver, other techniques such as refining were required (Bayley 1991; Bayley 2001). These methods can be divided into two distinct categories: the first separate the noble metals from the base metals and they include smelting followed by cupellation, and the amalgamation of gold from alluvial deposits with mercury; the second are methods used for parting gold from silver, which can be achieved by cementation with salt (Ramage and Craddock 2000), by using sulphur or antimony sulphide, and from the late Middle Ages onwards, with mineral acids (Bayley 1996).

Technical developments in mining and smelting continued throughout Roman times and led to the routine exploitation and use of noble metals during the Middle Ages. In Central Europe, famous argentiferous lead mines, e.g. in the Harz Mountains, the Erzgebirge, Rammelsberg, the Black Forest (Steuer and Zimmermann 1993; Goldenberg *et al.* 1996) to mention the most important ones, and others in southern Europe (Francovich 1993), were exploited for their silver throughout the medieval and modern periods. Gold ores were mined and smelted in Bohemia, the Alps, the Hohe Tauern Mountains (Günther and Paar 2000; Cech and Walach 2001; Cech 2007), Romania, and Iberia. By the early Renaissance, metallurgical techniques and operations used in gold and silver production were widespread knowledge and applied to various types of ores across Europe, culminating in their codification in various texts (see below).

The situation in Europe in the sixteenth century was erratic on various levels. Politically, the Austrian Empire was divided into many provinces controlled by either feudal or ecclesiastical powers, lowering the influence of the central authority. On religious matters, the Lutheran Reformation was spreading widely, intensifying divergence among European populations. The discovery of the New World, and the trade with Asia, created a fundamental change in many peoples' mind, opening it up for the vast potential of 'discovery', but also deeply upsetting established economic and political realities. Great technological advances took place since the Middle Ages, partly thanks to economic changes, resulting in increasing production, capital investments in industries, and transfer of knowledge between craftsmen. These technological developments were also possible due to a progressive cultural movement that increasingly relied on the power of humans, through experiment and observation, to push forward the limits of knowledge, which led to a related gradual change in the perception of nature. This laid out the foundations for the creation of modern science.

Metallurgy, chemistry and alchemy in the sixteenth century were overlapping fields with blurred boundaries. More precisely, alchemy and chemistry were not separated at that time, but were one arena, which is increasingly suggested to be called '*chymistry*' to avoid terminological and semantic confusion (Newman and Principe 1998; Martinón-Torres 2005: 36-39; Martinón-Torres and Rehren 2005a). This term has been adopted for this research, as it was considered particularly

appropriate in the study of the laboratory of Oberstockstall (see below). Chymists and metallurgists, despite sometimes following very different purposes for their activities, shared common operations and this is frequently acknowledged by historical sources (Szabadváry 1992; Newman 2000; Martinón-Torres 2005: 48-51; Martinón-Torres and Rehren 2005a). Among their common activity, fire assay in particular played a crucial part in the development of both disciplines.

2.1.2. Fire assay: an essential tool in metallurgy

When a gold or silver-bearing deposit was found, it was (and still is!) fundamental to know its richness in noble metals in order to decide whether it was worth exploiting. For this, small but representative amounts of this ore have to be analysed to determine quantitatively its content of precious metals. This analytical technique is called assay. Several assaying techniques have been known and used for centuries in metal making and working: specific gravity, touchstone, and fire assay. Specific gravity is the measure of the density of a material, which is determined using the principle of Archimedes. The assay with the touchstone was usually applied to alloys and compared visually the colour of the streak made on the touchstone by an unknown gold alloy to that of a reference alloy of known composition.

Fire assay is based on the same physico-chemical principles as smelting, but is done on a much smaller scale (Agricola 1556; Hoover and Hoover 1950: 220). It combines a series of slag-forming, oxidising and reducing operations to transfer any noble metal possibly present in the ore into a quantity of lead metal. From the latter, the noble metals are then extracted by cupellation. One major difference with smelting, besides the smaller scale, is the accurate weighing of the initial sample of ore or metal/alloy to be assayed, and of the final product, to calculate at the end of the operation the exact proportion in precious metals. As fire assay is one of the main foci of this project, this is explained in more detail later, when presenting the descriptions of high-temperature procedures related to the metallurgy of precious metals in sixteenth-century written sources (cf. chapter 4).

After cupellation, one further step called parting may be required when silver and gold occur together – which frequently happens in the case of gold ores – to separate them. This can be done by cementation – a high-temperature solid state process, probably first used by the Lydians in the sixth century BC (Ramage and Craddock

2000: 12-13, 181-183) – or, after the Middle Ages, with a wet process using mineral acids (Bayley 1996).

The Middle Ages were a period of increasing demand in metals, fast exhausting the known deposits. Besides, at the beginning of the Renaissance, noble metals were arriving in large quantity from the New World, competing with the metal production of the Old World. It became necessary for the miners of the Old World to find and mine low-grade deposits and develop more reliable quantitative systems of analysis to evaluate these poor ores (Rehren 1997). A main result was the increasing use of fire assay in the late Middle Ages as an analytical technique to fulfil these new requirements (Rehren and Eckstein 2002). The techniques for small-scale assay and refining of precious metals developed greatly during the Renaissance in the overlapping fields of mining, minting, and chymistry, to mention only the main ones. Fire assay was common practice during the sixteenth century for various metals and became essential for gold and silver.

Fire assay can be used for different purposes. The first one, which is of interest to prospectors and miners, is to calculate the quantity of gold or silver in an ore, or of both, as they often occur together as a natural alloy called electrum. There is unambiguous evidence for assaying in the context of mining and smelting at the medieval silver mine of Brandes-en-Oisans, France (Bailly-Maître and Bruno-Dupraz 1994; Bailly-Maître 2000; 2002), and in the sixteenth century in the Kodlunarn Island, Canada (Unglik 2000; Beaudoin and Auger 2004), and at Münster in the Black Forest, Germany (Schifer 1998). One cupel from Montbéliard, France, dated to the late sixteenth-early seventeenth century, also seems to point towards the fire assay of ores (Thomas *et al.* 2006). The practice of fire assay is also relevant for metals such as copper or lead, which might contain gold and/or silver. Finally this is of great use in the minting industry to assess the quality of coins and detect potential debasement and fraud. Examples of this are known from the Archbishop's palace in Trondheim, Norway (Saunders 2001) and at the Tower of London (Bayley 1996), as well as for the illicit practice of minting at Pymont, France (Jeanjacquot 1993). Broader implications of fire assay have been its essential role in the discovery of elements and the development of analytical chemistry. As Smith stresses in the introduction to the translation of Ercker's book, "the assayer collected a large portion of the data on which chemical science was founded" (Sisco and Smith 1951: xv).

2.1.3. The Renaissance metallurgical texts

Some references to high-temperature metallurgical techniques can be traced back to Antiquity (Bailey 1929; 1932; Gunther 1959; Osbaldeston and Wood 2000). However the first detailed and accurate descriptions of various methods and processes are found in Theophilus' *On Diverse Arts*, written in the twelfth century. In particular, cupellation in the context of silver and gold refining is explained accurately for the first time in this book (Hawthorne and Smith 1979: 96-97; Bayley 2008). This was followed by numerous treatises in the sixteenth century, such as the anonymous *Bergbüchlein* and the *Probierbüchlein* (ca. 1500 for the first and ca. 1520 for the second; Sisco and Smith 1949), Biringuccio's *De La Pirotechnia* (Biringuccio 1540; Smith and Gnudi 1990), Agricola's *De Re Metallica* (Agricola 1556; Hoover and Hoover 1950) and Ercker's *Treatise on Ores and Assaying* (Ercker 1580, 1st edn 1574; Sisco and Smith 1951). These manuscripts explain the techniques, tools, equipment and processes applied for mining, smelting, assaying and refining of most known metals, and especially of precious metals. Although at the time they represented an unprecedented effort of clarity and detail (Long 1991; Long 2001), from a present-day perspective they can sometimes appear confusing and in some cases relatively imprecise. Besides, they may reflect recipes, witnessed by an individual author, which did not match actual widespread industry and laboratory practices of the sixteenth century. In most cases, it would therefore be precarious to rely only on sources of that nature to fully reconstruct past technologies and cultures. This points out the fact that the pre-modern metallurgy of gold and silver needs a more detailed understanding because of the variability and versatility encountered in its practice. This research aims to make an original contribution to Renaissance archaeology and history by addressing this question.

The recipes and procedures explained and recommended in the main three sixteenth-century technical texts mentioned above, which are relevant to the metallurgy of precious metals, will be presented in further detail later in this thesis (cf. chapter 4). As already mentioned, one aspect of this research is to compare the results from the archaeometric study of archaeological material excavated from specific historical contexts, which informs about practical processes, to relevant contemporary written descriptions.

2.2. Archaeological sites

The two main sites relevant to this study are the small-scale Renaissance laboratory of Oberstockstall and the contemporary smelting site of the Angertal (Fig. 2.3). Both sites have been extensively excavated and large quantities of different materials, artefacts and debris have been found, which have shown that these sites were connected to metallurgy, especially to precious metals as will be argued later (cf. chapter 5 and 6).

Fig. 2.3. *Map of Central Europe in the sixteenth century showing the location of the Oberstockstall laboratory and the Angertal gold smelting site (modified after Roberts 1991: 146).*

2.2.1. Oberstockstall: a chymical and metallurgical Renaissance laboratory

2.2.1.1. The laboratory of Oberstockstall and its intriguing owners

The archaeological site of the sixteenth-century laboratory is situated in the manor house or castle of Oberstockstall (Fig. 2.4) in the village of Kirchberg am Wagram in Lower Austria (Fig. 2.3). This property was mainly built in the sixteenth century as an expansion of the building and chapel erected in the fourteenth century.

Nowadays, the Oberstockstall manor house hosts a restaurant and wine cellar, and the sixteenth-century collection from the laboratory is exhibited in the *Museum Der Alchemist* in Kirchberg am Wagram.

Fig. 2.4. *The Oberstockstall chapel (photo: M. Martinón-Torres).*

The activity in the Oberstockstall laboratory is dated to the second half of the sixteenth century. The year 1548 was scratched on a glass disc found in the archaeological record and provides a *terminus post quem* for the period when the laboratory was set up. Its end probably happened between 1585 and 1590, the latter being the year of an earthquake which occurred in Kirchberg am Wagram and may have caused the destruction of the laboratory (Von Osten 1998). During this period, the Oberstockstall castle was owned by four parsons, two pairs of brothers: the Trenbachs and the Fuggers. All four could have been potential users or patrons of the laboratory according to the chronology and to their various interests in metallurgy, chymistry, and astronomy. A brief portrait of each of these individuals is therefore given here, as they will set the historical background of the site and help in the interpretation of the archaeological evidence.

The *Trenbecken-Chronik* is the main source for the history of the Trenbach family. It was first translated by von Osten (1992b), and parts of it have subsequently been published by herself (Von Osten 1998) and Soukup and Mayer (1997), both books being the main sources for the following descriptions unless otherwise cited. Christoph von Trenbach (1511-1552, Fig. 2.5, left) was the first to be associated with this particular laboratory while he was canon of Passau and

Kirchberg from 1538 until 1552. His main achievement was the refurbishment and expansion of the castle in 1548 during which the sacristy and the room above it, which would serve as "laboratory rooms", were incorporated. It is not known for certain whether the laboratory was ready and/or used under Christoph von Trenbach's ownership, and whether he himself performed experiments there. All we can say is that he bought numerous chemicals, tools and books and left a huge debt when he died in 1552, part of which was owed to the apothecary in nearby Krems, news of which was received as a surprise as he was regarded as wealthy. This debt may have resulted from his investment in expensive technical instruments and tools to use in the laboratory and perform chymical and metallurgical operations, or perhaps rather from the developments of the edifice, but also because he paid his younger brother's studies at various universities in Austria and Italy. In any case, there is no doubt that this debt was, at least in part, due to the local chemist. Some hypotheses regarding this debt and the circumstances of von Trenbach's death are discussed by von Osten (1998); different arguments are also proposed by Soukup and Mayer (1997). In any case, it is suggested that instead of dying of the plague, which had widely spread in the region at that time, Christoph von Trenbach could have died from either chronic poisoning by lead or mercury (Von Osten 1998: 92), or a remedy composed of antimony (Soukup and Mayer 1997: 11). The mention of antimony might be of some importance in light of the results of the analysis of the archaeological material recovered in Oberstockstall (cf. chapters 5 and 7).

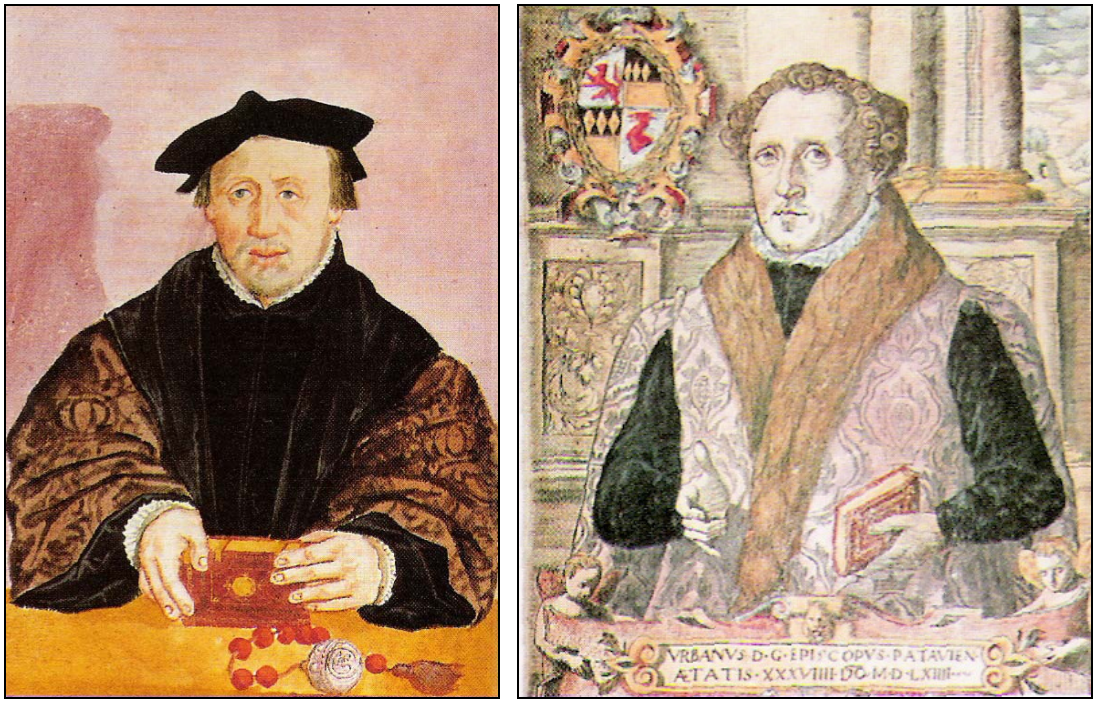


Fig. 2.5. *Christoph von Trenbach (left) and Urban von Trenbach (right) (after Soukup and Mayer 1997: 150).*

After the death of his brother in 1552, Urban von Trenbach (1525-1598, Fig. 2.5, right) became the new canon of Kirchberg and undertook to pay his brother's debt. He was interested in art and science and studied geomancy and chiromancy at university. He was in favour of the Reformation and showed enthusiasm to the protestant doctrine. It is not known whether he himself used the chymical and metallurgical laboratory of Oberstockstall, but it seems that he protected the operations performed there during the time of his bishopry (Soukup and Mayer 1997: 15). The Trenbach chronicles do not really explain the function of the laboratory at that time, but there was clearly some activity going on there (Von Osten 1998). Urban von Trenbach was interested in chymistry; this was shown by his allowing the use of the laboratory, whatever this was for, and this was also expressed by his perseverance in obtaining a manuscript attributed to Paracelsus, famously known for his interests in physics, botany, and chymistry, amongst many other science-related topics. On the other hand, he was also familiar with metallurgy, as he operated a mint between 1563 and 1577, after he had left his Oberstockstall office. This could suggest that he performed or supervised metallurgical processes while he was at Oberstockstall and got his first experience in metallurgy there. He

was appointed bishop of Passau in 1561 and therefore probably left Oberstockstall around that time.

From 1564 to 1570, the occupier of Oberstockstall was Balthassar Ottenberger von Grubhofen, priest of Kirchberg am Wagram. He does not seem to have personally played a major role in the history of the laboratory, at least according to the written sources available.

1570 sees the beginning of the Fuggers era in the Oberstockstall castle, with the appointment of Viktor August Fugger (1547-1586, Fig. 2.6, left) as canon of Kirchberg. It is of some relevance here to specify that the Fuggers have been an important German family since the fourteenth century, and to tell more about them in the context of metallurgy and mining. They played a crucial part in trade and politics in Europe since the late Middle Ages, and had close relationships with European emperors and kings, lending them money for diverse purposes; they also liaised regularly with the Church and the Pope. The Fuggers exploited copper and silver mines in Austria and other areas in Central Europe from the end of the fifteenth century onwards, and became the "most influential financiers of their time" (Ehrenberg 1928: 83) at the beginning of the sixteenth century. This considerable wealth and power originated mainly from financial loans; mining shares and trade of goods, such as metal ingots were, however, far from negligible. This continuously increasing business lasted until around 1550. Then it started to decline mainly due to debts and a lack of business abilities of the third generation of Fuggers to manage such a substantial economic empire. At the time of this decrease in wealth and loss in influence in the economy and politics, Viktor Fugger's father (Hans (Johann) Jakob Fugger) left the business after a strong quarrel with the rest of the family (Ehrenberg 1928: 124). It is relevant to note that Johann Fugger was more interested in art and science than business, and became one of the most important patrons and book collectors of his time. Later he worked for Ernst von Bayern, who was deeply fascinated by and involved in chymistry, and carried out experiments in his own laboratory (Soukup and Mayer 1997: 17). Viktor Fugger may therefore have been young when in contact with chymistry for the first time. He seemed to have a particular interest in Paracelsus, similarly to Urban von Trenbach, attested by the fact that he was later dedicated a manuscript by a famous paracelsist of his time (Soukup and Mayer 1997: 20-22). This could have influenced his activity in Oberstockstall and led him to practise chymistry or even *chrysopoeia* – the transmutation of base

metals into gold. Nonetheless, he might have used this laboratory for more mundane metallurgical procedures such as the analysis of ores, knowing earlier generations of his family got their fortune from the exploitation of metals. He perhaps did both. What can be assumed is that, once again, this owner of the Oberstockstall castle was interested in metallurgy and chymistry.

Fig. 2.6. *Viktor A. Fugger (left) and Sigmund F. Fugger (right) (after Soukup and Mayer 1997: 19-27).*

After Viktor Fugger, his brother Sigmund Friedrich Fugger (1542-1600, Fig. 2.6, rght) became the new landowner of Oberstockstall in 1586. However, Sigmund Fugger did not come to Oberstockstall as priest of Kirchberg am Wagram before 1589, due to his duties as canon of Salzburg. There is not enough information about the relationship between Sigmund Fugger and his estate in Oberstockstall between 1586 and the earthquake in 1590 – which may have caused the destruction of the laboratory – to suggest that he was involved in any metallurgical and/or chymical activity there. However, it seems plausible that he was one of the users or protectors of this laboratory, for he was involved in metallurgical activities prior to taking office in Kirchberg am Wagram: he struck coins in the early 1580s while he was in Salzburg; and later he employed a famous alchemist (Michael Polhaimer) in 1594-95

after he had left Oberstockstall (Soukup and Mayer 1997: 24-30), which indicates that Sigmund Fugger as well had a connection with chymistry and metallurgy.

This brief presentation of the major characters involved in the history of Oberstockstall between the middle and the end of the sixteenth century is fundamental to understand the context of the various activities undertaken there and the significance of the material recovered. The connections and acquaintances of these parsons may also be of importance: namely, Dr Wolfgang Kappler, Christoph von Trenbach's apothecary and doctor, who was supporting the use of antimony-based remedies; the scholar Konrad Gesner and the paracelsist Michael Toxites in close relationship with the Fugger family, and the duke Ernst von Bayern who knew Urban von Trenbach and Sigmund Fugger (Soukup and Mayer 1997: 17).

All in all, this microcosm appears to portrait the spirit of the European Renaissance, with religion, politics and economic enterprises inextricably linked, all coupled with an aristocratic interest in erudition and practical experimentation that would, in the long run, lead to a renewed understanding of the natural world. This underlines the importance of the archaeological remains excavated in the sacristy of the Oberstockstall chapel, and the value of their thorough study.

2.2.1.2. Archaeological context

The laboratory located in the sacristy of the Oberstockstall manor (Fig. 2.7-2.8) was excavated first in 1980 and then again in 1993-94 (Von Osten 1998; Fig. 2.9). This work was undertaken on request of the present owner of the estate after he had started digging, concerned about the stability of the floor but also apparently eager to discover a potential treasure hidden in the ground (Martinón-Torres 2005: 76). More than a thousand ceramic and glass sherds and artefacts together with residues of chemical and high-temperature reactions, charcoal, ashes, leather and bone pieces, were found in what was identified by the archaeologist von Osten (1992, 1998) as a waste pit (Fig. 2.10). The base structures of two furnaces were also located, indicating that the sacristy was the very room where high-temperature operations were performed. This assemblage appears to have been constituted between 1548 and 1580/90, this period being identified by a single coin, a date on a dish and dendrochronological analysis (Cichocki 1998).

The material collected from both excavation seasons has been comprehensively catalogued and macroscopically described and classified by von Osten (1992a; 1998). Some preliminary study and a few analyses have also been performed (Soukup and Von Osten 1991; 1992; Von Osten and Soukup 1992; Soukup and Mayer 1997), but systematic investigation remained necessary in order to get a clearer picture of the activities carried out in this chymical and metallurgical laboratory during the second half of the sixteenth century.

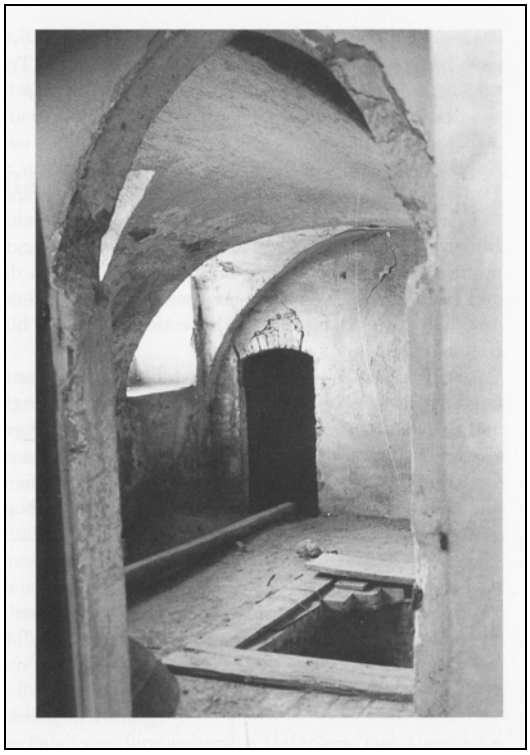


Fig. 2.7. *Picture of the sacristy showing the excavation pit, as seen from the chapel (Von Osten 1998: 17).*

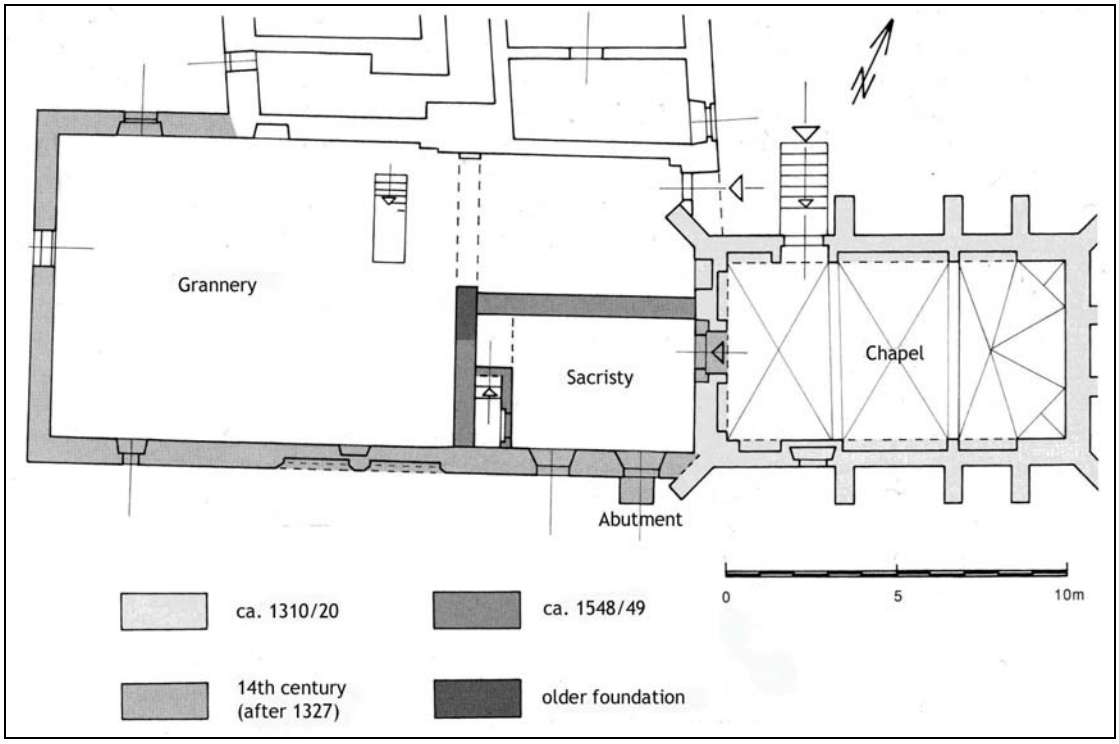


Fig. 2.8. *Plan of the sacristy in the Oberstockstall castle (after Martinón-Torres 2005: 78, modified after von Osten 1998: 17).*

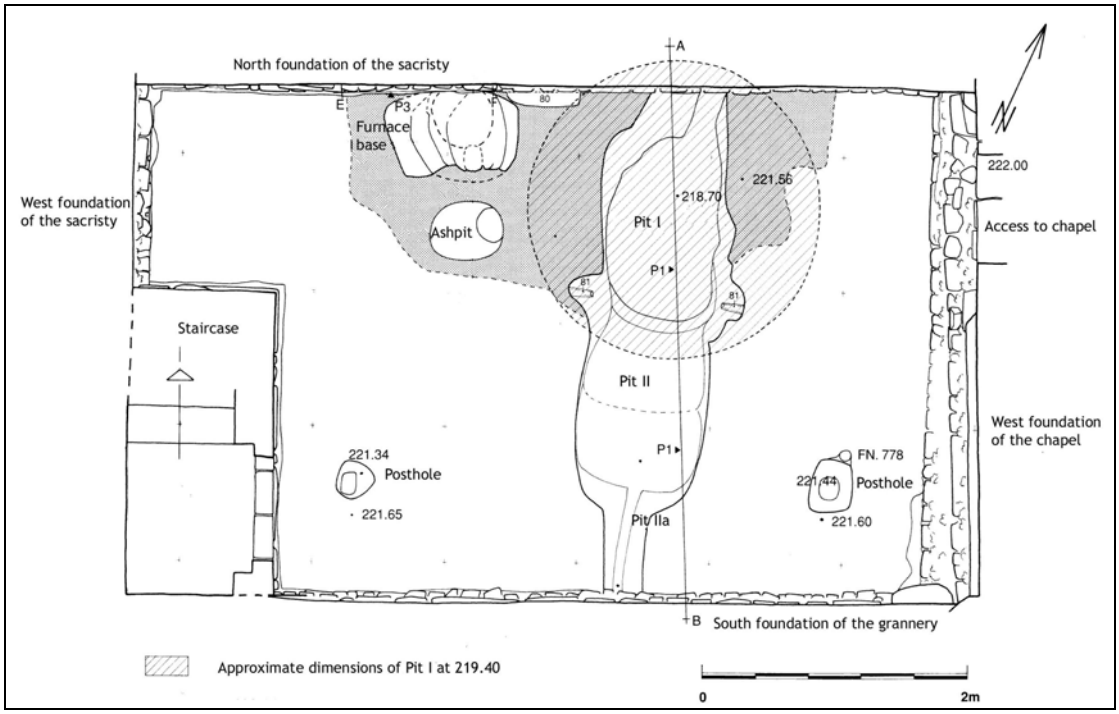


Fig. 2.9. *Plan of the excavation of the sacristy (after Martinón-Torres 2005: 78, modified after von Osten 1998: 22).*

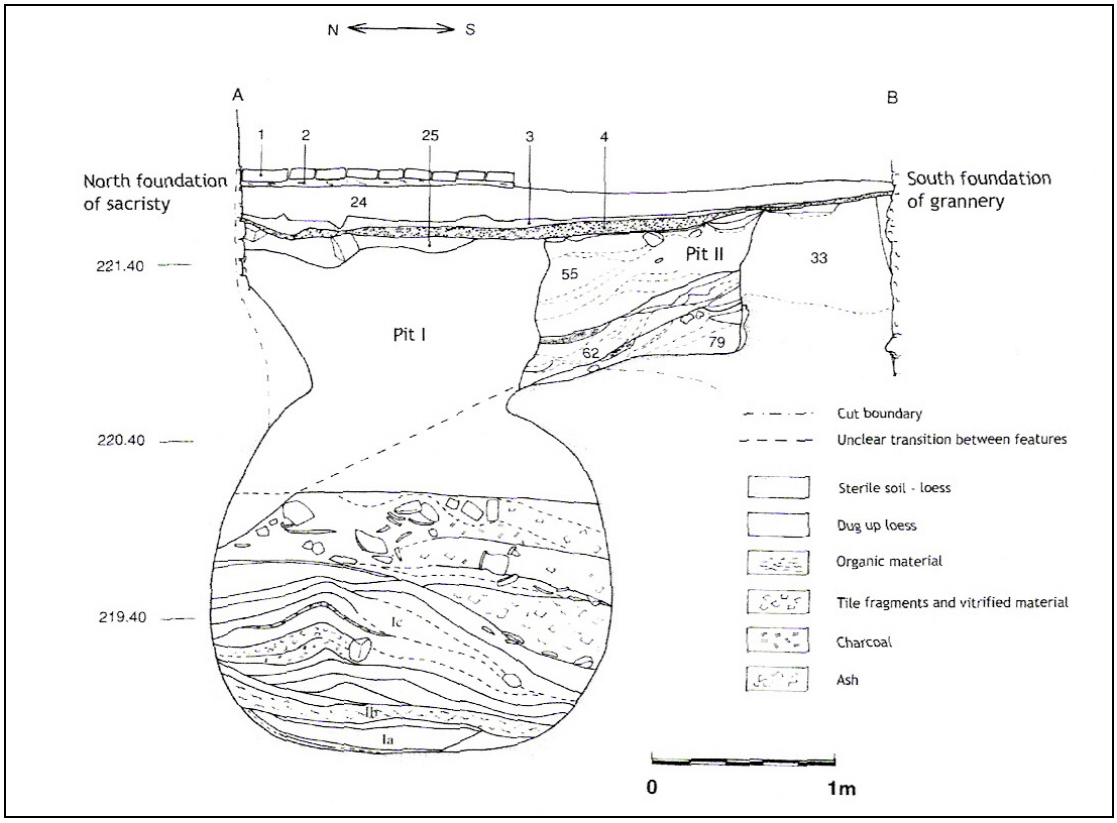


Fig. 2.10. *Excavation pit where most of the laboratory assemblage has been found (after Martinón-Torres 2005: 79, modified after von Osten 1998: 20).*

2.2.1.3. Archaeological material: technical ceramics and metallurgical remains

This section only gives a very brief introduction to the high-temperature ceramic reaction vessels, their metallurgical residues, and various specific separate products clearly associated with the activity undertaken in these ceramics, as part of this material has already been extensively studied (Rehren 1998; Martinón-Torres *et al.* 2003; Martinón-Torres 2005; Martinón-Torres and Rehren 2005b; Martinón-Torres and Rehren 2009) and the main presentation of the artefacts relevant to the present project is given in the section dedicated to this site (cf. chapter 5). As will be seen, this archaeological assemblage mainly includes ceramic reaction containers most likely used in dry high-temperatures processes – namely triangular crucibles, scorifiers and cupels –, among other glassware and ceramic vessels more specific to wet and low-temperature operations such as distillation, sublimation or for general use in a laboratory. Phials, alembics, sieves, funnels, distillation receptacles, still heads, cucurbits, sublimation capitals and one distillation column are examples of

objects found in Oberstockstall and possibly used in these low-temperature reactions (Fig. 2.11).

Fig. 2.11. *Various ceramic and glass apparatus from Oberstockstall, diagnostic of a laboratory (scale bar 15 cm) (after Martinón-Torres* et al. *2003).*

The nearly three hundred triangular crucibles (Fig. 2.12) are made of very refractory clay usually with graphite inclusions, allowing them to withstand heat and chemical reactions. The *ca.* sixty scorifiers (Fig. 2.13) are flat open vessels, very versatile, and manufactured with alumina- and quartz-rich clay, relatively thin walled and possibly used in oxidising reactions. The ash cupels (Fig. 2.14) are thick vessels with a shallow depression on the top, with a porous body made of a mixture of finely crushed bone and wood ash. They were used for cupellation – a high-temperature process which separates noble metals from lead by oxidising the latter into litharge, which is then being absorbed by the cupels, while the former remain on the surface.

***Fig. 2.12**. Triangular crucibles from Oberstockstall (scale bars 5 and 15 cm) (after Martinón-Torres 2005: 105).*

***Fig. 2.13.** Scorifiers from Oberstockstall (scale bar 15 cm) (after Martinón-Torres 2005: 141).*

***Fig. 2.14.** Cupels from Oberstockstall (scale bar 5 cm) (photo: M. Martinón-Torres).*

Comprehensive research has been performed on the ceramic vessels mentioned above; this research now focuses on the remains produced by high-temperature chemical and metallurgical reactions within these vessels. Two types of occurrence of these remains have been identified: some residues still attached to the vessels (Fig. 2.15); and fragments of slag, metal and matte probably produced in some of these

vessels but later removed from them (Fig. 2.16). These products and waste materials have been thoroughly described and analysed (cf. chapter 5), as they will help understand the use of the vessels, and hopefully enable to reconstruct the metallurgical operations, performed in them. To the best of my knowledge, this study is arguably the first to this extent on such material.

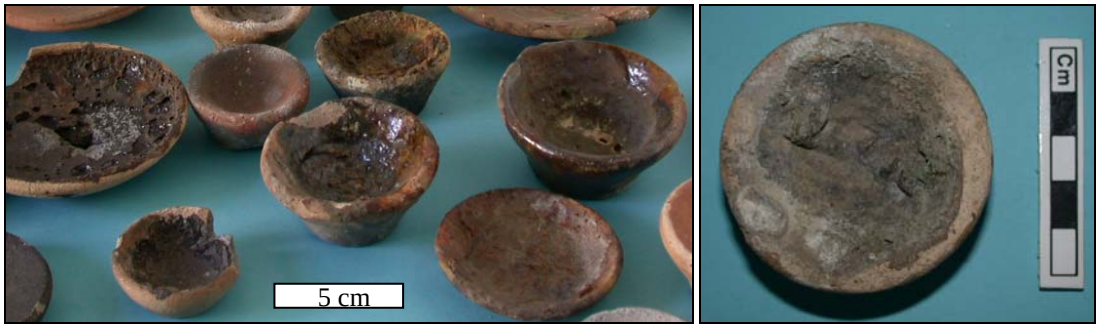


Fig. 2.15. *Metallurgical residues within scorifiers (scale bars 5 cm) (photos: M. Martinón-Torres).*

Fig. 2.16. *Various types of metallurgical residues, including fragments of metal, matte and slag (left, scale bar 5 cm); Example of a triangular matte cake (right, scale bar 5 cm) (photos: M. Martinón-Torres).*

2.2.2. The Angertal: a major sixteenth-century gold smelting site

The introduction to this site is mainly based on publications written by Cech (Cech and Paar 1997; Cech 2000; Cech 2007), the archaeologist in charge of the survey and excavation, and Walach, who is a geophysicist with a particular interest in the field of mining and archaeometry (Cech and Walach 1995; Cech and Walach 1998; Cech and Walach 1999; 2001). Further accounts about the history, mineralogy, and geology of the Hohe Tauern region are also included in order to better understand the situation of the whole area and more particularly of the Angertal site

in this region (for instance Ludwig and Gruber 1987; Moosleitner 1994; Günther 1994; Günther and Paar 2000).

A brief presentation of the surrounding mining sites of the Bockhart and the Erzwies will precede the main section on the Angertal. These two mining sites are of interest here since they will provide the geological and mineralogical background of the region and, more importantly, because they were most likely potential ore suppliers for the smelting site of the Angertal, especially during the relevant period of this study, i.e. the sixteenth century.

2.2.2.1. Brief historical account of the Gastein region

The gold smelting area of the Angertal valley is located in the Gastein region, south of the state (*Bundesland*) of Salzburg in Austria (Fig. 2.3). The Angertal is close to the mining areas of the Bockhart and the Erzwies, which are part of the Hohe Tauern mineralisation and mining complex and where there is wide evidence for a long history of exploitation of gold and silver ores. These mining areas of the Hohe Tauern were connected to smelting sites in the valley through established pathways; this was the case also for those located in the Anger river valley, i.e. the Angertal. While the mining of the various ores in the Bockhart, and most likely in the Erzwies as well, took place all year round, the smelting operations occurring in the Angertal were seasonal. According to the historical records, the ore was transported from the mines to the smelting sites in the valley using bags made of pigskin, which were slid down the slopes of the mountains. The tracks left by such transportation are still visible today, running from the Erzwies to the Angertal (Cech 2007: 177).

The first period of exploitation of gold in the Gastein region seems to occur between the middle of the first millennium BC and the end of the fifth century AD During these early times, the gold is likely to have been extracted from river sand and placers. Nonetheless, even though the region was known to be rich in gold, the extensive mining of the Bockhart gold-bearing veins only started during the fourteenth century and ended at the end of the nineteenth century.

The earliest written reference to the smelting site of the Angertal goes back to the end of the fourteenth century (Cech and Walach 1999). Smelting of ores extracted from mines in Gastein, such as those located in the Bockhart and the Erzwies, took place from that period until the end of the sixteenth century (Cech and Walach

1999). The smelting site of the Angertal was probably abandoned around that time, perhaps because of a lack of wood, which was needed to produce the charcoal used as fuel in the smelting furnaces (Cech and Walach 1999). Another most likely possibility for this halt of the activity in this smelting area seems to have been the exhaustion of the rich veins up in the mines, which may be inferred by the fact that after the heyday of activity of the sixteenth century, no exploitation to such a scale took place, although there are signs that prospecting continued during the following centuries. Although the smelting took place over a much longer chronological period than that of the laboratory in Oberstockstall, the peak of smelting activity at the Angertal site could be assumed from written sources to take place in the 1550s-1560s, as this is the period of highest production in the whole Gastein-Rauris region (Gruber 2000: 165), and is therefore contemporary to the period of activity at Oberstockstall. One interesting fact is the mention of the Fuggers as part of the major investors in mining exploitations of the Gastein-Rauris area at the end of the fifteenth century (Gruber 2000: 162), which provides an anecdotal – yet direct – connection between the two sites addressed in this thesis.

2.2.2.2. Archaeological context and material of the Bockhart and Erzwies mining sites

The excavation of the Bockhart site revealed the existence of different mining phases dated to the fifteenth and sixteenth centuries. Miners' living quarters from both periods were discovered, as well as a large smithy dated to the sixteenth century (Fig. 2.19) and an ore dressing plant, with ore stamp mills (Cech and Walach 1999; Cech and Walach 2001; Cech 2007). In the area of the smithy were found numerous iron tools – mostly broken – and nails, as well as many pieces of smithing slag (Fig. 2.17) (Cech and Walach 1999; Cech and Walach 2001: 290-293; Cech 2007). These slag fragments would have been produced by the smith when making, amending, or repairing iron tools for the miners. The excavation of the smithy also revealed a probable small assay furnace with fragments of black platy slag (Fig. 2.18), which are clearly different in appearance from smithing slag and share a striking macroscopical resemblance to that from the Angertal, which result from a smelting process (Fig. 2.21). The presence of a structure such as a small assay furnace is not surprising at a mining site, since it enables to regularly test the ore extracted from the veins to assess its richness in precious metals, as advised by most sixteenth-century

authors (Hoover and Hoover 1950: 219; Sisco and Smith 1951: 9-10; Smith and Gnudi 1990: 136). This small furnace sits on top of the iron finds, which had fallen from the shelves when they collapsed, and were scattered on the floor of the smithy; thus, this structure most probably belongs to a later phase of ore prospecting rather than indicating the ongoing monitoring of ore quality.

The material selected from the excavated site of the Bockhart mainly consists of pieces of ores from various locations, marked on the map of the site presented in chapter 6 (Fig. 6.4, p. 193), platy slag, probably associated to the assay furnace, and iron smithing slag, most from the main period of activity, i.e. the second half of the sixteenth century, although some of the pieces of ores may belong to a later prospecting phase, possibly also associated to the assay furnace.

These two types of slag were analysed to confirm their technological origin, the first coming from the smithing process, and the latter probably from a late assaying process associated to the assay furnace located in the smithy. The results from these analyses have not been included in the more extensive presentation of the data on the Angertal material, since they are not directly linked to the smelting process and would not give any relevant additional information for the reconstruction of the metallurgical reaction or be discussed in relation with other questions asked for this research. It is, however, worth mentioning that smithies have been documented from similar mining contexts in the Black Forest (Goldenberg 1993).

Fig. 2.17. *Fragments of smithing slag of various sizes. These were found east of the smithy, further than the slag heap (BO 442, scale bar 5 cm; photo: A. Mongiatti).*

Fig. 2.18. *Typical platy slag found at the Bockhart. Note the remarkable similarity between this slag and the main type of slag found in the Angertal (Fig. 2.21) (BO 364, scale bar 5 cm; photo: A. Mongiatti).*

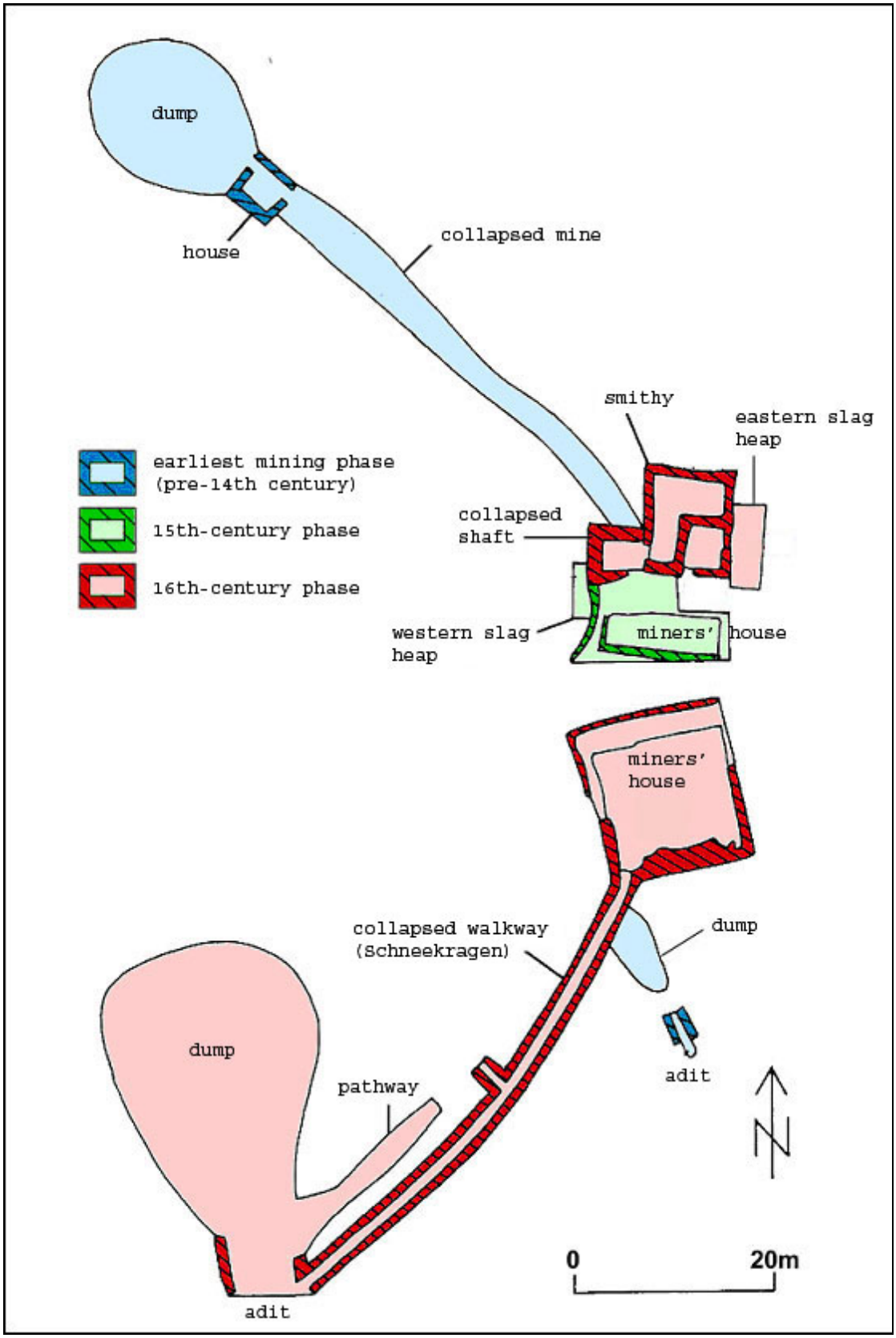


Fig. 2.19. *Map of the excavated mining site in the Bockhart (modified after Cech 2000; Cech and Walach 2001).*

Similarly to the Bockhart mines and also close to the Angertal smelting sites are the ancient mines of the Erzwies, known to have been exploited for their gold and silver since the Middle Ages (Gruber 2000). The main mineralisation in these deposits includes gold-rich sulphides crossing iron carbonate ores, such as ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$) and siderite ($FeCO_3$). Some veins of lead and zinc sulphides can also be found (Strasser 1989; Cech 2007: 3-14). Several ore samples from both mining sites were studied to determine their nature and variety, and confirm whether they were potential ore suppliers for the Angertal smelting site.

2.2.2.3. Archaeological context and material of the Angertal smelting site

In 1996, a comprehensive geophysical and geomagnetic survey of the Angertal smelting area combined with other archaeometric and archaeological studies was undertaken to draw detailed maps of the region, and precisely locate the smelting sites. Several potential positions for smelting installations were identified and found to be present in various states of conservation. One of these smelting areas, which presented unique and very good preservation, was selected for further excavation, which took place between 1996 and 1998.

The excavation brought to light three well-preserved furnaces; several slag heaps of different sizes; a dry stone wall, which separates one major slag heap from the furnaces and probably protected the working area from potential landslides; and a few wooden beams which were interpreted as being part of the water-powered bellows system of the furnaces (Fig. 2.20). The material uncovered mainly consisted of a vast amount of various smelting furnace and waste materials, ore fragments, and charcoal pieces. These are all metallurgical remains characteristic of the technology performed at this site. Their nature, quantity and degree of preservation made this site ideal to investigate the large-scale smelting technology of gold and silver ores during the Renaissance, and from this basis try to understand the wider socio-economical context and implications of this metallurgical activity in the region.

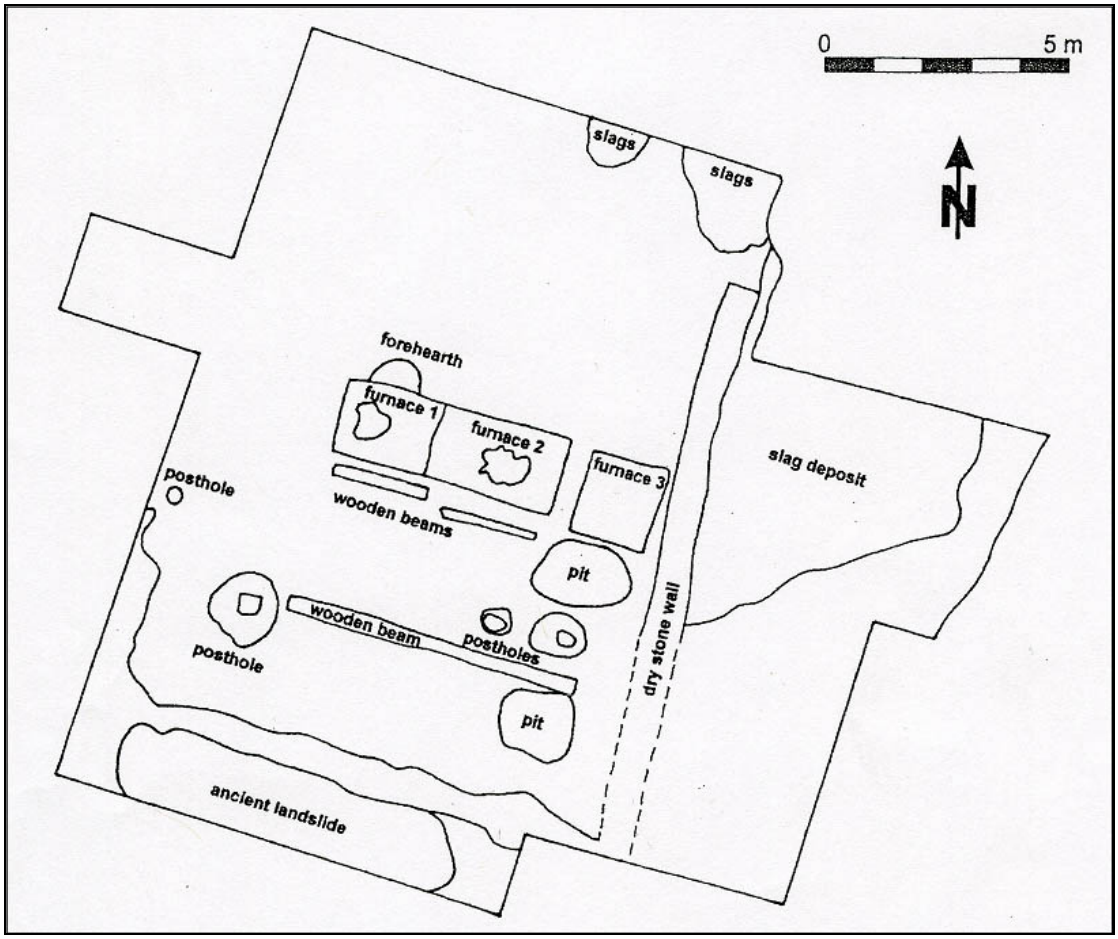


Fig. 2.20. *Map of the Angertal smelting site after excavation (after Cech and Walach 2001).*

The material selected for the current project, according to the sampling strategy explained in the next chapter (cf. chapter 3), has been documented and catalogued. Most of the material excavated at the Angertal smelting site consists of a large quantity of slag of various types (Fig. 2.21), some matte and several pieces of ore and furnace wall. Some fragments of lead bullion have been discovered attached to agglomerates of various other materials such as matte and/or slag. One particularly interesting find was a furnace bottom, most likely a stone slab forming the base of furnace 3, of which a cross-section revealed a trapped bullion-matte-slag sequence. This was of special interest, as it preserved the three main products of this furnace in direct contact and unquestionable common origin, and therefore was in detail sampled and analysed (Fig. 2.22). As will be seen in the chapter presenting the results of the analytical study of the Angertal material, this furnace bottom and other slag samples from specific contexts proved useful when investigating the organisation of the site and the way the three furnaces were operated (cf. chapter 6).

These fragments of metallurgical remains were subjected to microstructural and chemical study following the same procedure (cf. chapter 3) as for the Oberstockstall assemblage, to allow full and direct comparison of the results.

Fig. 2.21. *Examples of various types of slag from the Angertal smelting site, the majority being platy (left) and others displaying a more bulky appearance, due to the possible agglomeration of several pieces of slag together with soil materials (right) (scale bars 5 cm, photos: A. Mongiatti).*

Fig. 2.22. *Section (left) and top view (right) of part of a furnace bottom (scale bars 15 cm, photos: A. Mongiatti).*

In order to be able to interpret the data as meaningfully as possible, it is appropriate to consider some theoretical concepts relevant to this project, so as to establish a framework to study metallurgical technology in the sixteenth century.

2.2.3. Theoretical framework for the scientific study of archaeological and technical materials

2.2.3.1. Contextual studies for chymistry

One major aim of this study is to understand past metallurgical processes and reactions within the specific cultural and technological system in which they took place. This science-based archaeological study needs to bear in mind the historical context of the case studies considered when explaining the results of such a scientific research and suggesting intentions behind facts, in order to avoid anachronistic interpretations (Martinón-Torres 2005; Martinón-Torres and Rehren 2005a). The Renaissance perception of matter was indeed different from our own, and it is critical to acknowledge this when looking at archaeological materials and technologies. Despite apparent similarities, processes will most likely not have been carried out with the same mental framework by a sixteenth-century chymist or metallurgist as by a modern scientist. In the changing era of the Renaissance, there were variations and differences in the way of looking at materials and objects, depending on very diverse criteria such as social and cultural contexts, professional background, or purpose of the operations. A good example is shown by Renaissance chymists, some of whom believed that *chrysopoeia* and *argyropoeia* – the transmutation of base metals into, respectively, gold and silver –, was not a conceivable operation, while others believed it was feasible and repeatedly attempted to produce gold.

Alchemy and chemistry have generally been studied separately by historians from different schools of thought. Historians have often wondered whether alchemy – in its modern meaning following the definition given in Diderot and d'Alembert's *Encyclopédie* of 1753 – was to be regarded as a science or as a philosophy (Principe and Newman 2001; Martinón-Torres 2005: 40-48) and therefore the extent to which it contributed or not to the history of chemistry and science. However, it appears that when looking at both disciplines in the sixteenth century, this differentiation cannot be made and alchemy cannot be studied "as a uniform and constant monolith" (Principe and Newman 2001: 419). To avoid these biases in the historiography, Principe and Newman (2001) suggested to rewrite this history on the foundation of specific case studies and therefore on contextual investigations rather than doing "broad surveys of alchemy" (Principe and Newman 2001: 419).

In the case of Oberstockstall, closely linked to chymistry, it is therefore crucial to refer to the temporal and cultural contexts when interpreting the results from the archaeometric and archaeological study and suggesting intentions and purposes behind practical and technical actions. Also in the Angertal, even though the ultimate purpose of the metallurgical operations may be easier to infer, we cannot assume that their understanding of the process was the same as ours. Overall, this epistemological framework highlights the need for high-resolution contextual studies such as these presented here.

2.2.3.2. The study of past technology

Technology can be defined in various ways, which has led to divisions in the methodologies applied to its study (Ingold 1999; Schiffer and Skibo 2001). After a long period of 'static' investigation of technology, which was restricted to the artefacts or to some extent, to acts, but considered as purely technical and practical (Ingold 1990; Dobres 2000), new approaches have emerged to incorporate the human agent (Schiffer and Skibo 1995; 2001) and therefore give a 'dynamic' dimension to the notion of studying past technology. One such approach is that of the *chaîne opératoire*, which is not only a mere description of a "series of technological operations which transforms a raw material into a usable product" (Cresswell 1990: 46), but also takes human beings, society, and culture into account (Sellet 1993: 106; Dobres 1999: 125). It seems then that embedding the study of technology in the concept of the *chaîne opératoire* could avoid these notional dissensions and lead towards more interdisciplinary research (Martinón-Torres 2002). In the case of the assemblages from Oberstockstall and the Angertal, one primary aim is to correlate disconnected materials and tools into a technological sequence, always bearing in mind the context in which these materials were found. The use of the *chaîne opératoire* seems therefore a useful strategy here when trying to ascertain both practical knowledge and intentions, as long as present-day perceptions and assumptions are not directly applied to past technological sequences.

It is increasingly acknowledged that the anthropological component of technologies is as important as their material element (Lemonnier 1993; Stark 1998; Dobres 2000). Technologies are largely influenced by human agents, who have to be regarded both as individual and social. Even though limitations due to various

practical and technical constraints do exist, the particular knowledge, skills and intentions of humans together with their social and cultural environment greatly influence their technological choices (Lemonnier 1993; Dobres 1995; Sillar and Tite 2000). The purposes behind objects and techniques may be directly reflected in the material culture when technological styles can be identified, and artefacts and their manufacturing technologies can be seen as a medium of personal and social expression (Lechtman 1977; Lemonnier 1993; Ingold 1999). However, when this is not so obvious, the interpretation may be clarified by combining historical studies with archaeological research. Such an approach is intended to be applied to both archaeological sites in this project, and completed by the scientific analysis of archaeological materials. The full integration of the context of each site should allow an optimum interpretation from the combination of history, archaeology and science (Martinón-Torres 2008).

This research project will therefore aim first at reconstructing processes embedded and interpreted in specific contexts, and building on this, at more widely contributing to the history of technology and science taking into account the various approaches introduced above, in order to avoid the direct application of modern presumptions, and therefore misinterpretations, to the past.

2.2.4. Summary

This chapter has introduced the historical and archaeological background to the sites addressed in this thesis, namely the small-scale laboratory of Oberstockstall and the large-scale smelting site of the Angertal, both located in Austria and showing a major period of activity taking place in the sixteenth century. Besides outlining the types of technical instruments and debris to be studied, it has been argued that their technical study should be contextualised in their specific socio-cultural framework, in order to avoid simplistic or anachronistic interpretations. In particular, a *chaîne opératoire* approach has been justified as a means to research these case studies while recognising the diversity of concepts of nature that existed in Europe during the Renaissance. It is hoped that these case studies will contribute to a growing picture of Renaissance technology and science that is created as a sum of parts rather than a monolithic survey.

Chapter 3 – Methodology

This science-based archaeological project combines a critical literature review of sixteenth-century metallurgical texts with an archaeometric study of archaeological finds from the Oberstockstall laboratory and the Angertal gold smelting site. The present section introduces the sequence of steps taken for the scientific analysis and the analytical instruments employed. First, relevant excavated remains had to be chosen from both archaeological assemblages. These selected finds were then visually characterised in order to be documented and recorded, and identify ideal locations for invasive sampling. When sampling was deemed appropriate, small specimens were then mounted in epoxy-resin blocks to be prepared for microscopic study and compositional analysis. A good number of powder pellets was also produced for elemental bulk analysis in the case of the Angertal smelting site and its associated areas. The microstructural and chemical study is primarily based on reflected light optical microscopy, scanning electron microscopy with an attached energy dispersive spectrometer (SEM-EDS) and energy-dispersive X-ray fluorescence (ED-XRF). Electron probe micro analysis-wavelength dispersive spectrometry (EPMA-WDS) and non-destructive micro X-ray fluorescence analysis (μXRF) were also applied to resin mounts when necessary. The reasons for the use of these instruments will be explained in this chapter. Details of the sampling and analytical protocols are also given below.

3.1. Selection of archaeological finds

Different selection levels of the archaeological material occurred within the frame of this project. The first one concerned the broad choice of remains, which appeared relevant to address the research questions raised within this project. This initial decision was based on various parameters: the diversity of the finds, their peculiarity, and – when the same kind of material was noticed repeatedly – the quantity, in order for their analysis to be representative. Following the broad macroscopic assessment, more precise criteria were considered for the selection of objects or fragments that would be sampled invasively for further analytical study. The criteria for these two stages of selections were different from one site to the other and these differences will be pointed out below.

3.1.1. The Oberstockstall laboratory

The material recovered from the Oberstockstall Renaissance laboratory presented a great amount and variety of archaeological remains but all of them from a discrete, well-dated context: a waste pit containing material used between 1548 and 1590. There were *ca.* one thousand objects, including around three hundred crucibles, sixty scorifiers and one hundred cupels. These are the most abundant objects, and the ones showing evidence of high-temperature use; most of the remainder of the equipment consists of containers and low-temperature distillation apparatus. A further fifteen to twenty metalloid lumps and sheets of metallic copper and lead were also part of this technical assemblage. A first selection of objects and pieces had been provided by the archaeologist in charge of the excavation (S. von Osten) for analytical study at the UCL Institute of Archaeology, and further significant fragments were brought back from Austria, partly for a now completed PhD project (Martinón-Torres 2005) but also with a view to a future study concentrated on residues of chemical reactions from high-temperatures processes. That first PhD focused on unused crucibles and scorifiers, though some used vessels were also included to assess their performance, and the cupels were published previously (Rehren 1998). The present research project studies the reaction vessels with clear evidence of high-temperature residues, as well as other metallurgical waste, whilst ensuring some overlap between this PhD and the previous studies aforementioned.

These finds were therefore readily available for study, and in enough quantity and variety to address the main issues and unknowns associated with this site. Of particular interest were all types of waste products, such as matte fragments or 'cakes', metal and slag pieces, and metallurgical residues within ceramic vessels bearing diagnostic traces of high-temperature use. Incomplete reaction containers including triangular crucibles and scorifiers (cf. chapters 2 and 5) were preferentially chosen, since they were better candidates for additional microscopic study, requiring invasive sampling; eleven triangular crucibles and thirteen scorifiers were sampled.

Despite the overall great quantity of finds, there were less than ten slag, metal fragments and matte 'cakes' in this assemblage. Furthermore, no reference studies could be considered here, as this unique archaeological material has no known parallels, both in terms of material consistency and complexity, and archaeological context, except for a much smaller but very similar assemblage recently discovered

and excavated in Kapfenberg (Friedl 2006), and which is currently under study (some initial results are presented and confronted to Oberstockstall in chapter 7). All of these 'cakes' and fragments were therefore selected for analysis due to their apparent diversity.

It needs to be pointed out here that the material studied only represents a very small fraction of the assemblage from Oberstockstall and even less of what might have been in use before the destruction of this laboratory. However, a good idea of the range of activities probably taking place at this site, could be reached, though we may not have acquired a full view of their variety.

3.1.2. The Angertal gold smelting site

This case study required a different approach. Considering the good preservation of the excavated site and the vast quantity of relevant material recovered, there had to be a careful selection of this archaeological material based on various parameters, and the finds from this site were thus chosen in collaboration with the site archaeologist (B. Cech). Here, as opposed to Oberstockstall, there was a broader range of spatial contexts, including several furnaces, waste pits, slag heaps, etc. Specific chronological relations between them were difficult to resolve, but the sampling selection was performed in order to ensure that all archaeological contexts were represented. Many fragments from different contexts were therefore chosen in order to show the multiplicity of materials at this site, characterise as much of the excavated area as possible and, when feasible, more than one piece was taken in order to be representative either of a particular location or a specific type of material.

The selected pieces are primarily fragments of slag of different sorts, furnace wall and lining, ore, matte, and metal. All these remains were recorded, weighed, documented and photographed. Since most of the slag and matte fragments showed similar features, thorough macroscopic examination of all finds was carried out to start choosing the finds that were subsequently sampled. This was completed by careful visual examination of the finds, and in many cases by non-invasive screening analysis of many of these pieces prior to sampling to avoid wasting archaeological evidence and analytical resources. The results from this initial qualitative investigation of chemical compositions by ED-XRF, which are not included in this document, led to the additional selection of several samples – when more than one

was present – from each chemical group to be sub-sampled, depending on the degree of homogeneity shown.

In contrast, some of the finds were considered specifically because of their distinct or unique appearance. They may not be representative of the entire activity taking place at the site, but they may nonetheless be important for the understanding of this site and could not be ignored.

To incorporate this particular site into its historical context, samples from the surrounding contemporary mining areas of the Bockhart, which has been excavated (Cech and Walach 1995; Cech and Paar 1997; Cech and Walach 1998; Cech and Walach 2001; Cech 2007) and the Erzwies, for which the pieces of ore were simply collected on the ground during a survey of the area, have also been included in this archaeometric study.

When excavation was taking place both at Oberstockstall and in the Angertal, not all materials could be identified by analogy with other studies because of their individuality. This first thorough investigation of new material will hopefully serve in the future as a reference study for other scholars excavating or characterising similar kinds of material, in addition to give primary and fundamental information about both archaeological sites.

3.2. Macroscopic description of the finds

This detailed examination involved a first macroscopic physical characterisation of the remains in order to record and document them. Some of these were drawn and all of them were photographed to allow for future reference and study.

The fragments were characterised in terms of external colour, shape, texture, etc. For instance, the colour of the post-depositional corrosion products of slag or matte cake might have been indicative of the potential metals inside, or some surfaces of the fragment could be original features and not result from breakage, and their shape characteristic of the inside of a particular ceramic vessel (Fig. 3.1).

Fig. 3.1. *Group of matte cakes from Oberstockstall showing very different and specific shapes indicative of the types of vessels in which they were produced (scale bar 5 cm; photo: A. Mongiatti).*

This three-dimensional observation of the archaeological remains by eye was completed by a more meticulous inspection with a stereomicroscope for the unique finds found in the laboratory of Oberstockstall. This microscope allowed a magnification from 6.4 to 40 times and it was thus possible to look more specifically at typical or particular features of the archaeological pieces. This also facilitated the identification of precise areas where the remains could be invasively sampled, in a way that would inflict the least possible damage to the original fragment or artefact but at the same time be enough to obtain as much information as possible. All sampling areas have been recorded because of the distinctiveness of such archaeological materials and in order to be able to interpret the results from their analysis in light of their physical location on the original artefact (Fig. 3.2).

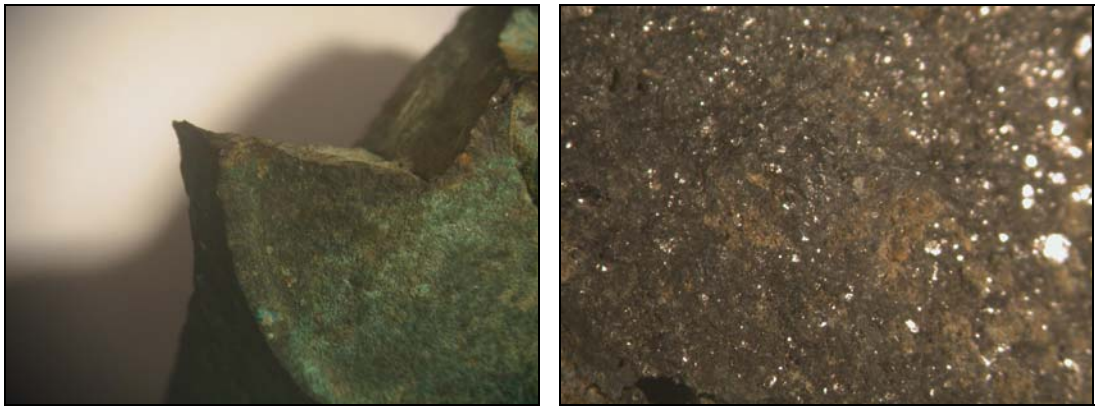


Fig. 3.2. *Left: pointing tip of a round matte cake, showing a relevant and relatively easily accessible sampling area; Right: rim of a triangular matte cake showing the graphitic fabric of a triangular crucible attached to it, giving information about the fabric type of the vessel in which this matte was produced (stereoscopic microscope, 60x).*

3.3. Invasive sampling of the selected pieces

In the case of the assemblage from the laboratory of Oberstockstall, small but informative fragments of crucibles and scorifiers with signs of use were cut in order to show both the ceramic fabric and the metallurgical residue attached to it together on a single cross section when mounting the specimens in resin blocks. Only sherds and incomplete or damaged vessels were sampled. From the slag and metal fragments, and the matte 'cakes', small and hardly visible pieces were removed, although ensuring these contained enough bulk material to be representative of the original find. In some cases, more than one sample was taken to distinguish any potential differences in the microstructure (gradient in porosity, in elemental concentration, in phase size, etc.).

For the large quantity of metallurgical waste from the Angertal, two samples were removed from each fragment, the first to be mounted in epoxy resin, in the same way as the specimens from Oberstockstall, in order to study the microstructure, and the other weighing between 15 and 20 grams to be ground to a fine powder and made into a pressed pellet for chemical analysis of bulk composition. The platy slag and matte from this site were thin enough to get the whole cross-section of the selected pieces in one resin block. Pellets of artefact samples from the site of Oberstockstall were not considered for bulk analysis due to the considerable amount of material required, which was not available from the objects of this assemblage, instead chemical analyses were done on the polished blocks, limiting the amount of

information available. Besides, the majority of the specimens from Obersockstall are mixtures of ceramic fabric from crucibles and scorifiers with metallurgical residues, thus a bulk analysis of crushed material would have been uninformative.

3.4. Sample preparation

3.4.1. Polished blocks of epoxy resin

The sub-samples selected for analysis were then mounted in standard epoxy resin for cross sections employing a 4:1 resin/hardener ratio. For both archaeological sites, the mounted samples were labelled following an established procedure, including a reference code made of the two initial letters of the archaeological site with a find number – when any existed – and a specimen number, e.g. OB 268/S1, a brief description of the artefact from which they were removed, the date they were created and the initials of the scientist who prepared them (Martinón-Torres 2005: 90). The specimens removed from metallurgical residues still attached to ceramic vessels from the laboratory of Oberstockstall and all but one artefact from the Angertal had find numbers, i.e. reference numbers of the archaeological contexts in which they were uncovered. On the other hand, metallurgical fragments not attached to ceramic vessels had not been given such an identification number, and thus new lists starting with OB S001 and AN N01 were created. This labelling system was also applied to the Bockhart and Erzwies ore specimens, using the find number as the identification number and adding a sample number – 01, 02 and so forth –, when more than one sample had been excavated from the same context, e.g. BO 991-07. The last part of the reference code /S1, /S2, and so on – referred to as the specimen number above – reflects the production of more than one resin block from one single artefact or sample or of one resin block and one pellet.

These mounts were then subjected to grinding using silicon carbide cloth under water at various grades (Grit 320, 600, 1200, 2500 and 4000), and polishing down to 1 μm particle size with an alcohol-based solution composed of a diamond suspension in cooling lubricant. Several specimens from Oberstockstall artefacts were polished down to ¼ μm, but it was soon realised that it was not particularly necessary in order to achieve a satisfactory level of polishing for both microscopic and analytical studies. Further noticing that it was creating some relief in such heterogeneous samples, this final step was therefore removed from the polishing sequence.

3.4.2. Pressed powder pellets

A relatively large quantity of material was cut with a tile cutter – ca. 15-20 grams – and first manually crushed to a fairly coarse powder with a hammer down to small fragments showing a particle size of around 2-3 mm. This coarse powder was then ground to a very fine powder (~ 50µm) using a planetary mill with counterweight during 10 minutes. The pots used for this fine grinding were either of tungsten carbide – sometimes detected by XRF analysis as contamination – or agate depending on the hardness of the material. The resulting powder was then dried at a relatively low temperature in an electric oven overnight.

This powder was subsequently mixed with wax – either kept in a desiccator or very briefly dried in an electric oven to remove any moisture – in an agate mortar and using a pestle to ensure complete mixing of the two materials. Both were weighed with a precision scale (+/- 0.0005 grams): 8.0000 grams of sample powder and 0.9000 grams of wax to obtain quantitative results when carrying out the elemental analysis. The mixture was finally pressed into a pellet at 15 tons for 3 minutes on average using a manual press in a 32 mm diameter mould.

3.5. Analytical study of the mounted specimens

3.5.1. Stereoscopic microscope

Many of the mounted specimens were first inspected with a stereomicroscope, specifically in the case of Oberstockstall because of the nature of the material, which is relatively new and unprecedented. This provided information on the texture: inner porosity, bulk colour(s), interface slag/ceramic, and reflectivity, which will be considered in the light of the data resulting from the analyses (Fig. 3.3).

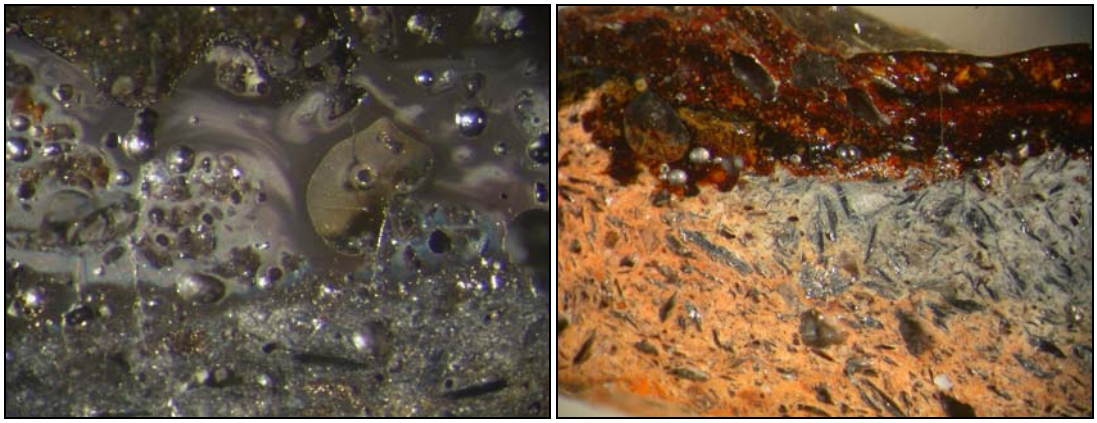


Fig. 3.3. *Grey and porous slag adhering to the dark grey graphitic ceramic fabric of a crucible (left: OB 345/S1, stereoscopic microscope, 40x, long axis ~4 mm) and dark red slag on top of the orange and grey ceramic fabric of a scorifier (right: OB N006/S1, stereoscopic microscope, 25x, long axis ~6 mm).*

The main techniques used for the analytical and microscopical study were reflected light microscopy, SEM-EDS, EPMA-WDS and XRF. The combination of these analytical techniques was considered ideal because of their applications in our particular case – detailed below – and of the minimal damage done to the selected archaeological material. Besides, this allowed methodological consistency with the previous work done by Martinón-Torres and Rehren on the crucibles, scorifiers and cupels from Oberstockstall, which also used these three complementary techniques (Martinón-Torres *et al.* 2003; Martinón-Torres 2005; Martinón-Torres and Rehren 2005b; Martinón-Torres and Rehren 2009).

3.5.2. X-ray fluorescence

3.5.2.1. Energy dispersive X-ray fluorescence

The principle of this analytical technique consists of a sample placed under vacuum and hit by high-energy X-rays in which the generated excitation of the atoms results in the emission of various signals, including element-specific fluorescent X-rays. These X-rays released by the sample are detected by means of a semiconductor crystal and transformed into a spectrum of intensity vs. energy through the computer software. By comparing this spectrum to a database of spectra of standards, the elemental composition of the sample can be determined (Pollard and Heron 1996; Veldhuijzen 2003). The instrument used at the UCL Institute of Archaeology was a Spectro Xlab 2000, with a rhodium tube and operating at 40kV. Two methods, called “Turboquant” and “Alloy”, both developed at the UCL Institute

of Archaeology for this instrument and set up with specific standards and polarising targets, have been used for the detection of oxide concentrations, i.e. stoechiometrically with oxygen, and of pure elements respectively. The "Turboquant" method was mainly applied to the qualitative analysis of cross sections and to the quantitative analysis of slag pellets, where all elements are likely to be oxidised, while the "Alloy" method was ideal for the analysis of matte samples and the detection of gold and silver if present in very small amounts in ore or slag samples. The former method gives non-normalised concentrations, while the latter is set by the software to normalise the results. For each method, all the elements are detected either as oxides or as elements but not as a selective mixture of both; this was taken into account as a possible issue when analysing samples containing both sulphides and oxides.

Prior to sample selection and preparation, all samples from Oberstockstall and many from the Angertal were first subjected to ED-XRF screening analysis without any sample preparation, which provided initial information about the bulk composition and allowed the identification of potential trace elements. In the case of the laboratory, because the original samples presented very irregular and corroded surfaces, this technique proved only useful on a qualitative level, to get a first idea of the elemental composition. It was also a crucial technique to detect and recognise elements such as gold and silver when present in minute amounts.

This non-invasive qualitative analysis was performed directly on various relatively large (~1.5 cm in diameter) areas of the remains. As suspected, this technique could not answer all of my questions and needed to be combined with invasive analytical methods. One reason for this was the low penetration depth of the X-rays in the sample, determining only the composition of surface layers a few micrometres thick, as is the case for the analysis of precious metals (Bachmann 1995). The penetration depth of the X-rays emitted by the source depends partly on the average atomic weight of the elements of the sample. Therefore, having metalloid fragments consisting mainly of relatively heavy elements such as lead, copper, silver, gold, and antimony, considerably reduced the depth of the area analysed. Furthermore, the surfaces of archaeological artefacts are typically severely altered in their composition by corrosion. Therefore, surface analyses can only give a first indication of the elements present, but not provide reliable quantitative data about the original chemical composition of the bulk.

A second screening analysis was applied to mounted specimens to obtain the chemical composition directly on a fresh cross section of the bulk. The problematic issue in that case was the small size of the specimens, which did not fully cover the detector window, therefore hindering a fine detection and reliable results. This second screening analysis was useful despite these limitations, as it offered basic chemical data, which informed the subsequent optical microscopy and facilitated phase identification prior to SEM-EDS and EPMA-WDS analysis (see below). It also gave trace elements information in the range of 10 to 100 ppm (0.001 to 0.01 wt %) not otherwise obtainable by SEM-EDS or EPMA-WDS analysis.

Finally, for a large number of samples from the Angertal smelting site and its associated mining areas, the Bockhart and the Erzwies, reliable quantitative data were produced thanks to the making and analysis of pressed powder pellets.

The precision and accuracy of the instrument were first assessed and then monitored by repeatedly analysing certified standards and reference materials of compositions similar to the archaeological samples. The reference data and measured results are detailed in appendix 1. For precision tests, the reference materials were always run with the samples, providing a set of several analyses for each of them. Their analysis gave good precision values, with coefficients of variation remaining for measurements in different days below 3% for major and minor oxides, except for lighter compounds such as soda and magnesia, and for sulphur, which can show higher variation when detected in low concentrations. Elements in concentrations below 0.1 wt% also show good results with coefficients of variation usually below 5%. With the exception of the above light compounds, the relative errors between the measured runs and the certified or reference values are generally lower than 15% for major elements and below 20% for minor elements, with occasional higher errors due to some possible matrix and mineralogy effects such as absorption, fluorescence or diffraction. However, in this thesis, all the comparisons of bulk compositions between samples use compositional differences larger than these margins, and they therefore remain significant.

3.5.2.2. Non-destructive micro X-ray fluorescence

The instrument used for this type of analysis was a Bruker (ex-Röntec) ArtTax spectrometer kindly made available by the Department of Conservation and Scientific Research at the British Museum. The excitation source of this instrument

is an air-cooled molybdenum X-ray tube with a maximum power of 40 W. The incident X-rays are collimated by a changeable collimator, for which the diameter can vary from 0.2 to 1.5 mm. All the analyses for this research were done with the 0.65 mm collimator, so as to allow comparability between the dimensions of the analysed areas of similar materials. This particular instrument provides a maximum high voltage of 50 kV and a tube current of up to 1000 μA. Analyses were carried out using the standard set-up of the instrument for metals, which applies a 50 kV voltage and 800 μA current. The detection of the X-rays is performed by a semiconductor detector, similarly to the ED-XRF instrument. The signal acquired is then amplified and the data is processed into a spectrum using a software called ArtTax 4.9. The calibration of the energy channels by fine tuning the peaks was carried out with silver used as standard. The quantification of the chemical data was further achieved through an in-house software, specially developed for metallurgical studies. A method called "High-silver", specifically designed for silver-rich materials, was selected and its calibration was established using the composition of four in-house standards, namely SB1, SB2, C2 and XF3, whose concentrations have been checked by Atomic Absorption Spectrophotometry (AAS) and are presented in the table below (Table 3.1).

	Ag	Au	Cu	Pb	Bi	Total
	wt%	wt%	wt%	wt%	wt%	wt%
SB1	90.13	4.87	5.00	b.d.l.	b.d.l.	100.00
SB2	85.06	9.95	4.99	b.d.l.	b.d.l.	100.00
C2	97.50	0.34	1.65	0.65	0.05	100.19
XF3	94.00	b.d.l.	6.00	b.d.l.	b.d.l.	100.00

Table 3.1. *Chemical composition of the standards used in the quantification method developed for the μXRF instrument by scientists of the British Museum.*

This micro XRF instrument was only used for the analysis of several beads obtained by experimental cupellation – the remaining three were mounted and analysed by SEM-EDS and EPMA-WDS –, there is therefore no issue of comparability between results. Besides, there is a good correlation between the results obtained with the scanning electron microscope and with the micro XRF instrument. This non-destructive technique was selected, as it did not require any sample preparation and could be applied directly to small areas of the beads,

allowing a quick and reliable analysis and the comparison between different areas of the surface. The beads analysed by micro XRF analysis were produced at a relatively late stage of this research and there would have been no opportunity to mount these in resin, this non-destructive technique was therefore seen as a good complementary method.

3.5.3. Reflected light optical microscopy

A metallographic study of the mounted specimens of the various metallurgical remains was performed using reflected light optical microscopy prior to SEM-EDS and EPMA-WDS analysis. Polished cross sections rather than thin sections were used here as the focus was placed on the opaque phases. Besides, thin sections are typically prepared on glass slides, which would prevent EDS analysis.

The characterisation of the polished cross sections in terms of their microstructure is as fundamental as their chemical composition, and proved to be essential for this research. This technique, exploiting the optical activity of the various phases in plane and cross polarised reflected light, was essential for the distinction of phases, which could not be consistently differentiated with the scanning electron microscope, even with the help of the wavelength dispersive spectrometer. This technique has been proved before to be almost indispensable for the study of polished cross sections of slag and metallic materials when investigating old metallurgical processes (Bachmann 1982).

Special consideration was given to the following features: general aspect; reflectivity; presence, size and distribution of porosity; shape (angularity); grain boundaries and interaction between the different phases; inclusions (distribution, size, shape). The microscope used was a Leica DM LM. Digital photographs were generally taken at magnifications 100, 200, 500, and 1000 both in plane and cross-polarised light (Fig. 3.4-3.5). Magnification 50 was applied in the case of the polished blocks of two beads obtained from experimental cupellation (cf. Chapter 6), in order to include as much of the sample as possible within the field of view.

Fig. 3.4. *Slag attached to the surface of a scorifier: long crystals of lead oxide in a lead silicate matrix, in plane polarised light (left) and in cross polarised light (right) (OB 269/S1, 200x, long axis ~650 µm).*

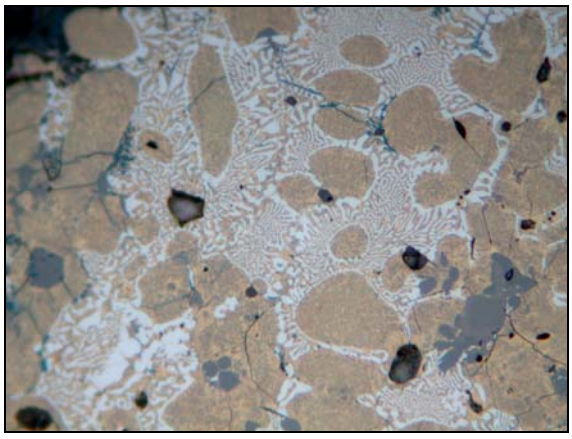


Fig. 3.5. *Dendrites of a eutectic mixture of lead sulphide and a copper- and iron-rich sulphide (AN 108-02, plane polarised light, 500x, long axis ~500 µm).*

3.5.4. Scanning Electron Microscopy

Two types of electronic beam instruments were used, a scanning electron microscope and an electron probe micro-analysis. The first instrument, mostly dedicated to the specimens from the Oberstockstall site, was a Philips XL30 Environmental SEM (ESEM) with an Oxford Instruments INCA spectrometer package and equipped with both secondary electron (SE) and back-scattered electron (BSE) detectors. For this type of analysis, the requirement for the samples was to be conductive; they were thus carbon coated, using a high vacuum evaporation and sputtering system. Pictures were usually taken both in SE and BSE modes (Fig. 3.6) at the same magnifications as the optical microscope to allow comparison (Fig. 3.7) between the images, and at higher magnification when necessary. The acceleration voltage applied to all analyses was 20 kV, the analytical distance 10 mm, the acquisition time 150 seconds, and the beam current set to reach a 30-40% dead time with a process time of 5 or 6.

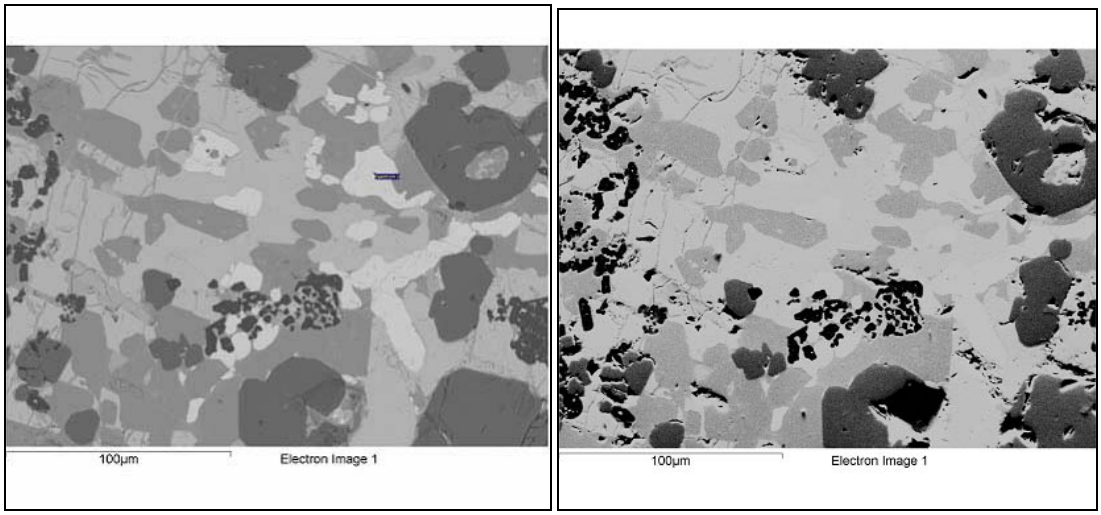


Fig. 3.6. *Photomicrographs of a matte cake in BSE mode (left) and in SE mode (right) (500x), showing the difference in atomic weight (the brighter, the heavier the element) in the former case and the topography in the latter. Topography in polished samples is typically low, and a residual BSE signal dominates the SE image.*

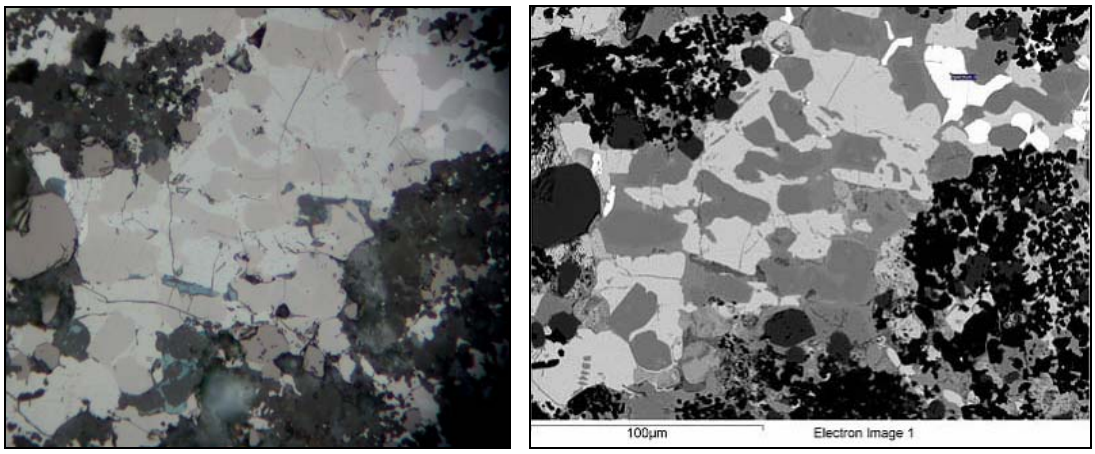


Fig. 3.7. *Photomicrographs of a matte cake in plane polarised light (left) and in backscattered electron mode in the SEM (right) (500x, long axis ~250µm).*

The electron probe micro analyser used was a JEOL JXA 8600 with an integrated operating system for the WDS analysis and a separate Oxford Instruments INCA software for the acquisition and processing of the EDS data, similar to the one fitted to the ESEM. This instrument was also run at an acceleration voltage of 20 kV, with a beam current of 10 nA giving a dead time of 30-40% for a process time of 5, and an acquisition time of 150 seconds,. All the samples from the Angertal smelting site were analysed with this equipment. In order to allow for comparability of results between both electron beam instruments, several samples from this site were analysed in both instruments and compared in terms of the concentrations of elements identified, to check that the values given by both microscopes and their

precision were in the same range. Several standards were also run in both to further ensure the validity of comparing the data. The results of these overlapping analyses have demonstrated a good agreement between instruments.

3.5.4.1. Scanning Electron Microscopy - Energy Dispersive Spectrometry (SEM-EDS)

The SEM-EDS was used for detailed structural inspection and local chemical composition analysis both of the bulk and of single phases. The principle of this instrument relies on the excitation of the specimen placed in a high vacuum chamber by an electron beam. The excited sample emits distinct signals at different energy levels, such as secondary electrons (SE), back-scattered electrons (BSE), transmitted electrons, X-rays, heat, etc. (Reed 1996; Watt 1997). The SE emission is indicative of the topography of the sample while the BSE signal gives an image of the chemical and phase composition. The energy dispersive spectrometer (EDS) detects X-rays emitted by the sample, usually by means of a semiconductor crystal. These characteristic X-rays result from the excitation of the specimen by the incident electron beam. For each element, these X-rays are always of a specific energy and characteristic of the elements present in the sample; they therefore allow their identification. By measuring the intensity of the characteristic energies for each element that has been detected, it is possible to determine their concentration. The association of these two types of data, the high-magnification imaging achieved and the high spatial resolution of the chemical information, made the SEM-EDS ideal for this research.

3.5.4.2. Electron Probe Micro Analysis - Wavelength Dispersive Spectrometry (EPMA-WDS)

WDS was available on the ESEM but the set-up of the WDS mode on this particular microscope and the duration of each analysis were too time-consuming for the rather large set of samples to be studied. In addition, the information gathered from the EDS proved to be sufficient in most cases. However, for a relatively large number of the Angertal samples, WDS analysis proved useful to resolve energy overlaps between important elements of the materials analysed, such as lead, arsenic and sulphur. WDS was readily available on the JEOL JXA 8600 and allowed relatively quick analyses compared to the ESEM. Wavelength dispersive spectrometry consists of a method to quantify the intensity of the X-rays of a specific

wavelength diffracted by a crystal. The wavelength of the characteristic X-ray and the crystal lattice spacings are related by Bragg's law and produce constructive interference if they fit the criteria of this law. Unlike EDS, WDS reads or counts only the X-rays of a single wavelength, not counting a relatively broad spectrum of wavelengths or energies. This generally means that WDS is able to identify quantitatively elements, whose energies closely overlap and which are in lower concentrations in typical energy dispersive spectra. A customised WDS method including twenty of the most relevant elements detected beforehand by EDS in various areas of the samples was therefore used for the Angertal specimens. The elements selected for this method included sodium, magnesium, arsenic, aluminium, silicon, phosphorus, sulphur, silver, potassium, tin, antimony, calcium, titanium, manganese, iron, nickel, copper, zinc, gold, lead. The three crystals were thallium acid phtalate (TAP), pentaerythritol (PET), and lithium fluoride (LIF); TAP was used to detect the K_α lines of the lighter elements (Na, Mg, Al, Si) and the L_α line of arsenic; PET for the K_α lines of P, S, K, Ca, and Ti and the L_α lines of Ag, Sn, Sb; LIF was used for the K_α line of Mn, Fe, Ni, Cu, and Zn and for the L_α lines of Au and Pb.

This scientific methodology, which includes the morphological description of the samples, their microstructural examination and chemical analysis, was used to study the assemblages of Oberstockstall and the Angertal, and to some extent samples from the Bockhart and the Erzwies. The results of this science-based investigation were then combined with a critical review of contemporary written sources, to compare the theory and practice of the metallurgy of precious metals. The interpretation of this data firstly aimed at identifying as much of the metallurgical chemical processes represented by the various finds as possible. These were then further discussed with the purpose of understanding the skills, intentions and ideas of the people performing the processes, and placing their activity into the wider socio-economic framework outlined in previous chapters (cf. Chapter 2).

Chapter 4 – The sixteenth century: a golden age for technical treatises

As introduced in the first chapter, one aspect of this project intends to use the information provided by the archaeometric study of archaeological assemblages and confront these results and interpretations to contemporary historical sources. This chapter introduces the three main relevant sixteenth-century metallurgical texts, which were considered for this comparison. This section further details the various methods and recipes proposed by the authors of the Renaissance with regards to the assaying and smelting of noble metals. As will be seen, these can vary greatly from one author to the other, and can sometimes be subjected to more than one definite technical interpretation in modern chemical and metallurgical terms.

4.1. Sixteenth-century metallurgical treatises and their authors

4.1.1. Written sources: a useful counterpart to archaeology

Written documents have always been useful to help interpreting archaeological data, whenever they were available. Pliny (Bailey 1929; 1932), and Dioscorides (Gunther 1959) are major references from Antiquity on various aspects, with several technical descriptions. A large number of later authors of the Middle Ages and the Renaissance regularly refer to and cite their work, especially Pliny's. The main technical manuscript of the Middle Ages is *De Diversis Artibus*, written by Theophilus during the twelfth century (Hawthorne and Smith 1979). This book gives the very first detailed explanations of techniques used in metalworking, glass making and glass working, among other topics. Looking more closely at the period of interest of this study, the sixteenth century appears to have been relatively prolific in terms of detailed technical texts, especially treatises related to metallurgy. This century started with the anonymous publication of two small manuscripts on mining, smelting and assaying, translated and published as a single book entitled *Bergwerk- und Probierbüchlein* (Sisco and Smith 1949). This document was followed by many other technical texts – also referred to as "books of secrets" – appearing in Renaissance Europe thanks to the discovery of the printing press and which would

play a significant role in the diffusion of technical knowledge and contribute to the development of modern science (Wolf 1935: 486; Long 1991; Eamon 1994; Long 2001). Amongst these, three major technical works on metallurgy, Agricola's *De Re Metallica* (1556), Biringuccio's *De Le Pirotechnia* (1540), and Ercker's *Beschreibung Allerfürnemisten Mineralischen Ertzt und Berckwerksarten…* (1580), would in some ways not be superseded for two hundred years (Wolf 1935: 486). The end of the sixteenth century saw the publication of Andreas Libavius's *Alchemia* (1597) and, the end of the following century, of John Pettus's *Fleta Minor* (1683) and Johan Conrad Barchusen's *Pyrosophia* (1698). Throughout this period, there was a plethora of technical writings on arts and crafts generally, and chymistry and metallurgy in particular.

4.1.2. The three main authors considered for this research

Vannoccio Biringuccio (1480-1539) was an Italian metallurgist and became famous by writing the earliest comprehensive treatise ever published about high-temperature metallurgical procedures, the art of metalworking, among other topics associated with the production of metals. This book is the well-known *De La Pirotechnia*, published after his death in 1540 and translated into English by Smith and Gnudi in 1959. This manuscript heralds the dawn of a "true technological literature" (Smith and Gnudi 1990: vii). Biringuccio collected information for this work from older written sources such as texts by Aristotle, Diodorus Siculus, Dioscorides, Pliny and Theophilus; but he also used his own experience, as he was in charge of an iron mine, and of the mint and arsenal of Siena, at the beginning of the sixteenth century. He also travelled across Italy and to Germany where he was able to witness metallurgical operations performed by craftsmen.

His work was followed by the most important book written by Georg Agricola, entitled *De Re Metallica*. Agricola (1494-1555) was a German scholar, humanist and man of science and his manuscript is a comprehensive treatise on mining, smelting, assaying, parting, and a variety of other technical operations carried out in the field of metallurgy. Agricola studied philosophy, physics, chemistry, medicine and natural sciences at the University of Leipzig and later in Italy. Back to Germany in 1527, he was appointed physician at the town of Joachimstal in the Erzgebirge, a very productive mining area of Bohemia. Between *ca.* 1530 and 1533, he travelled across

Europe to visit and study mines. In 1533, he was assigned physician for the town of Chemnitz, Saxony, another major mining centre, where he lived until his death. His whole life was dedicated to the continuous study of mineralogy, mining, metallurgy and science. Before writing his classic manuscript on metallurgy, Agricola published several books on various scientific subjects, which already made him renowned. Among them can be found *Bermannus* (1533), a small manuscript on mining terminology and mineralogy; *De Ortu et Causis Subterraneorum* (1544), the original book on physical geology; and *De Natura Fossilium* (1546) a comprehensive text on mineralogy. As most of his other books, *De Re Metallica* was written in Latin to ensure a learned readership; it was first published in 1556 after Agricola's death. It was translated later into German and Italian in the sixteenth century, and into English by Hoover and Hoover in 1912.

A third critical piece on metallurgy is Lazarus Ercker's *Beschreibung der Allerfürnemisten mineralischen Ertzt und Berckwerksarten…*, first published in 1574 and in a second edition in 1580. It was first translated into English by Sir John Pettus in the seventeenth century as part of his *Fleta Minor* (Pettus 1683), and then in 1951 by Sisco and Smith, *Lazarus Ercker's Treatise on Ores and Assaying, translated from the German edition of 1580*. Ercker (*ca.* 1530-1593) was a German chymist and metallurgist, about whom little is known. It is acknowledged that, during twenty years, he held different positions, and especially that of assayer, at various places such as Dresden, where he was first appointed in 1554, Goslar and Prague among the main towns he lived in. After 1567, he was in charge of the quality assessment of the coins at the mint of Kutna Hora. Through his various professional activities in the field of metallurgy, Ercker acquired a wide-ranging experience, which he transmitted in his manuscript, accurately describing metallurgical operations and instruments with more emphasis on the laboratory scale.

The following description of equipment, procedures and methodologies applied to both small-scale fire assay and large-scale gold smelting stems from these three major written sources of the sixteenth century, which influenced greatly the field of metallurgy.

4.2. Fire assay and its textual procedures

As explained in a previous chapter (cf. chapter 2), fire assay is the quantitative determination of metals in ores, alloys or other metallurgical products, using high-temperature chemical processes. Its principles and methods are overall supposedly similar to the large-scale metallurgical operation of smelting; only the scale and apparatus change (Agricola 1556; Hoover and Hoover 1950: 220). The sample assayed has to be representative of, and specific for, the ore deposits (or the metal or alloy analysed) in order for the results to be transferable to this larger scale. By far the most important of the ancient assaying techniques, fire assay considerably developed during the sixteenth century for gold- and silver-bearing ores, and has changed only in few details since then (Smith and Forbes 1969). For Agricola, fire assay is a comprehensive and necessary step for the miner, who can learn from it not only how much of the metal is present in the ore, but which minerals are richer in this metal and which fluxes will be most suitable to then smelt on a larger scale (Hoover and Hoover 1950: 219).

The assayer's equipment includes primarily wind- and muffle-furnaces, crucibles, scorifiers and cupels of different kinds, and balances of various precisions and sensitivities with their sets of weights. Additional equipment may consist of distillation apparatus, which could be employed to produce mineral acids to be used in gold-silver parting. Some of these instruments were recovered in Oberstockstall (Fig 2.11, p. 54) and suggest that parting was probably carried out in this laboratory. These would fit with the artefacts and products associated with fire assay studied in more detail for this project, but their analytical study falls outside the scope of this thesis.

This section presents the tools, reaction vessels and methodologies to be followed to perform fire assays, as they are presented in the three manuscripts introduced above. The equipment and procedures reported here are considered within the context of the present research and will therefore be described in the case of the fire assay of ores, bearing in mind that most descriptions are likely to be applicable to other types of raw materials.

4.2.1. Fire assay equipment

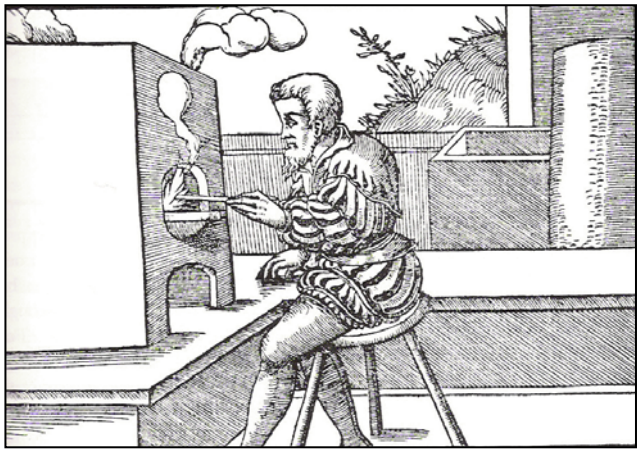


Fig. 4.1. *Rectangular assay furnace according to Agricola (after Hoover and Hoover 1950: 224).*

Small assay furnaces are normally rectangular in shape and usually built of brick (Fig. 4.1 and Fig. 4.2); they can sometimes also be of other shapes and made of thick iron sheet or clay reinforced with iron bars (Hoover and Hoover 1950: 224; Sisco and Smith 1951: 18-23). The main feature of one type of furnace is a platform, which separates the lower firebox from the chamber, where the reaction vessels are placed. The second type of furnace, in contrast, is described as having an empty space below the main chamber. The latter configuration uses the lower chamber for the circulation of hot air to the upper one, which therefore is both the firebox and the container for the reaction vessels. Both structures allow a good manipulation of the tools and control of the parameters of the reactions. The former minimises most the contamination of the charge in the vessels, which improves the accuracy of the reactions. The latter, using heating by convection, enables a better regulation of the temperature by means of hole plugs (Fig. 4.2, right), which can be inserted or removed to decrease or increase the airflow and therefore the temperature in the furnace. Many of these plugs have been found in Oberstockstall (Fig. 5.21, p. 130), and the remains of the furnace bricks showed a more intense vitrification on the top surface than in the bottom one, suggesting that they could have been of the second type of structure explained above.

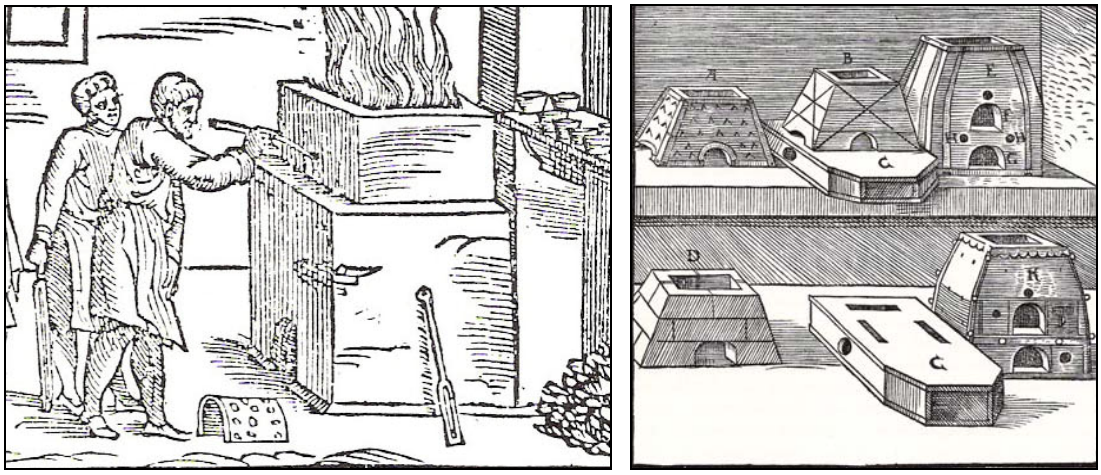


Fig. 4.2. *Assay furnaces as depicted by Biringuccio (left, after Smith and Gnudi 1990: 140) and Ercker (right, after Sisco and Smith 1951: 23).*

Muffles are made of refractory clay and their shape described as 'inverted gutter tile[s]' according to Agricola (Hoover and Hoover 1950: 227) with small openings (Fig. 4.3 and Fig. 4.2, left, at assayer's feet). They were put into the furnace to cover the reaction vessels, thus partially preventing fuel dust from contaminating the assay, and allowing the assayer to observe and manipulate the vessels inside the furnace. The muffles are usually as high as the furnace mouth and almost as long as the furnace chamber with some space kept between them and the furnace walls to put charcoal over and around them (Hoover and Hoover 1950: 227-8).

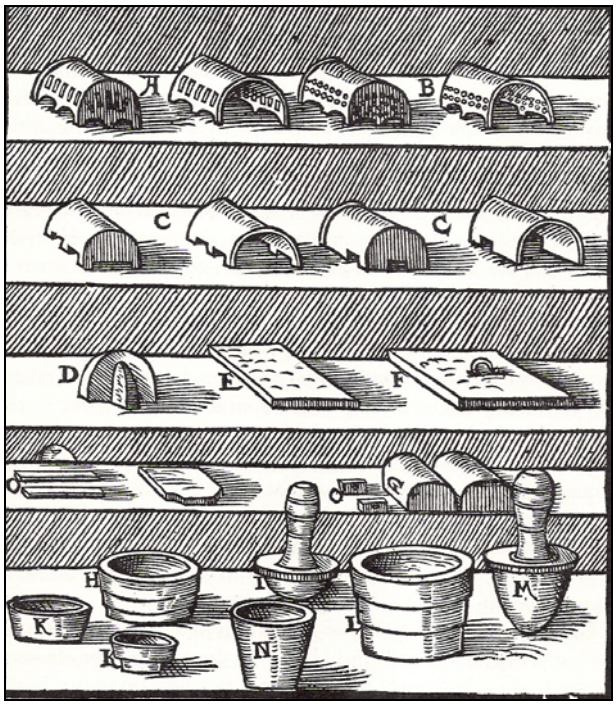


Fig. 4.3. *Laboratory equipment for fire assay: muffles in the upper half of the drawing, cupel moulds in the lower half (after Sisco and Smith 1951: 27).*

The assaying vessels are commonly used for small loads and are of three types: triangular crucibles, scorifiers and cupels (Fig. 4.4).

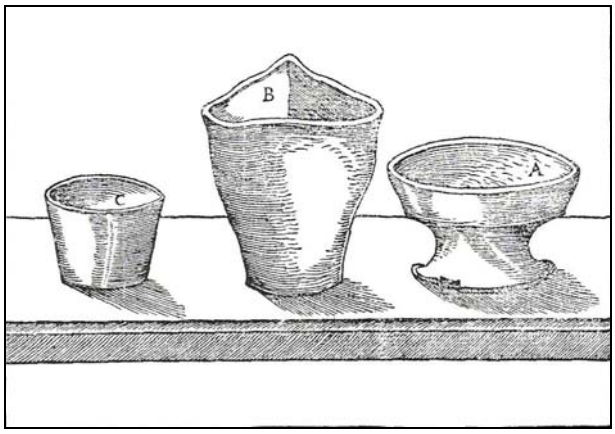


Fig. 4.4. *Cupel (C), triangular crucible (B) and scorifier (A) (after Hoover and Hoover 1950: 229).*

Triangular crucibles are described as being relatively thick walled and used for melting or smelting ores or metals under reducing conditions (Fig. 4.5). Their name is directly derived from their characteristic triangular shape, obtained by folding inwards the sides of a flat-based conical vessel, in order to produce a versatile and easily manipulated crucible with three pouring mouths.

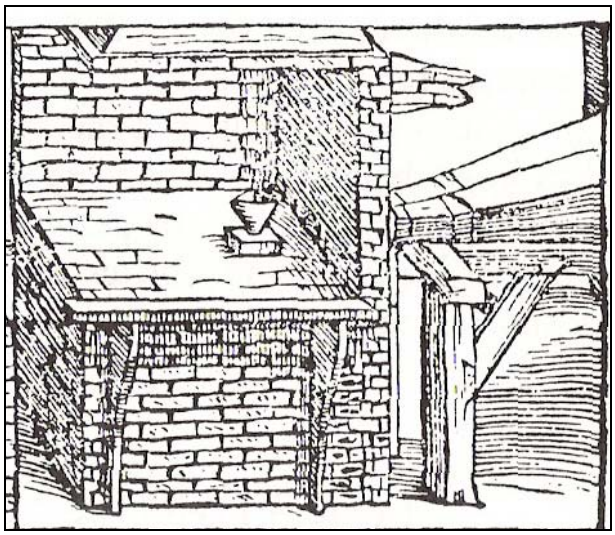


Fig. 4.5. *Melting in a triangular crucible (after Smith and Gnudi 1990: 292).*

Scorifiers are described by Ercker as moderately thick ceramic plates for melting ores or metals – among other general processes – under oxidising conditions (Sisco and Smith 1951: 25-27, 37-44). Agricola refers to them as a kind of 'crucibles' used only for the assay of gold and silver ores, as opposed to the other crucible type (triangular), which is used for the assaying of copper or copper ores, because they

usually have a larger volume (Hoover and Hoover 1950: 228). In any case, the main characteristic of scorifiers is that they typically exhibit a more open profile than ordinary crucibles.

All three sixteenth-century treatises give a very standardised depiction of cupels, these being presented as tray-shaped dishes with a very thick lower part. They are moulded in hollow wooden or bronze moulds (Smith and Gnudi 1990: 138) or in brass moulds which have no bottom (Hoover and Hoover 1950: 231) (Fig. 4.3 and 4.6). According to the three Renaissance authors introduced above, the best material to make cupels is wood or bone ash, which should be washed in water and dried in the sun or in a furnace, then moistened and ground. This ash must be as dry and free of impurities as possible when dampened and pressed with a pestle in the mould. Cupels are utilised for cupellation, to separate lead, and any other base metals present, from silver and gold by oxidation.

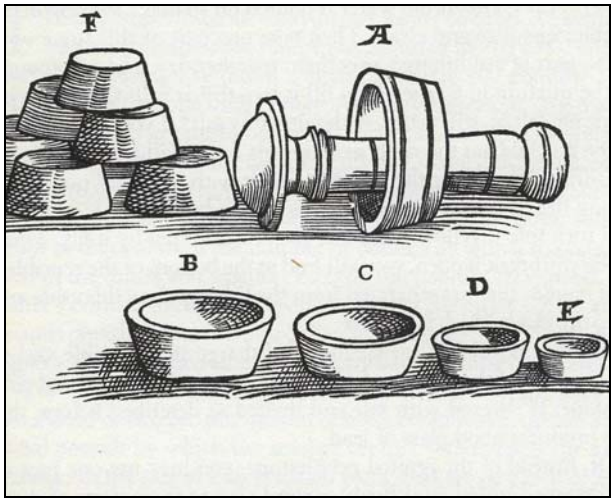


Fig. 4.6. *Cupels of different sizes with their mould (after Sisco and Smith 1951: 33).*

4.2.2. Fire assay methodologies

Biringuccio gives a general guideline for the assay of ores. If the ore is ‘pure’, i.e. it has been cleaned of its gangue components, the only necessary assaying step is cupellation with the addition of lead. If the ore is still mixed with some gangue minerals, then it is necessary to first melt it in a triangular crucible with lead and some fluxes, which are chemical reagents added to the charge in the crucible in order to lower its melting temperature, before it is cupelled (Smith and Gnudi 1990: 139-140). One interesting specification is the “strik[ing] of the bottom [of the crucible] several times against something” to help the mechanical separation of the various layers (Smith and Gnudi 1990: 140). Agricola agrees with the direct cupellation

process but only in the case of very rich silver deposits (Hoover and Hoover 1950: 244), while Ercker states that this is the only operation that gives the true silver content of an ore, and that it is suitable for any kind of silver-bearing deposit (Sisco and Smith 1951: 41-42). However, both Agricola and Ercker were aware of the slag formation, which happens when an ore that still contains some gangue is subjected to high temperatures. They therefore describe alternative ways to assay gold and silver ores, which involve a series of fusion reactions.

Two methods to perform the fire assay of ores are proposed by Agricola and Ercker. The first procedure consists of an oxidising fusion in a scorifier, also called scorification, followed by a cupellation step (Hoover and Hoover 1950: 239-241). The second one starts with a reducing fusion in a triangular crucible followed by scorification and a final cupellation stage (Hoover and Hoover 1950: 241-242). The two authors advocate the use of the first methodological sequence in the case of silver ores (Hoover and Hoover 1950: 244; Sisco and Smith 1951: 37-40), and both methods are considered as viable alternatives for gold ores (Hoover and Hoover 1950: 242-243; Sisco and Smith 1951: 112-114), with Ercker suggesting his preference for the former (Sisco and Smith 1951: 114). Agricola also recommends to carry out the assay simultaneously on more than one sample of the same ore to give a reliable result for the whole deposit (Hoover and Hoover 1950: 241). Ercker usually advises two assays to be performed simultaneously in the case of assaying for silver (Sisco and Smith 1951: 51, 59).

4.2.2.1. First method: scorification and cupellation

The sample of ore to be assayed is first finely ground and precisely weighed (Sisco and Smith 1951: 37, 112; Smith and Gnudi 1990: 140). Biringuccio and Agricola advise to pre-heat a muffle and reaction vessels – cupels and scorifiers – with charcoal in the assay furnace (Hoover and Hoover 1950: 239; Smith and Gnudi 1990: 139). Silver-free lead is then mixed with the crushed ore and charged into the hot scorifiers. Ercker and Agricola also suggest the possibility of first melting the lead in the hot container and then adding the ore in fractions on top of the lead (Hoover and Hoover 1950: 239; Sisco and Smith 1951: 39-40), and stirring together the lead and the ore with an iron rod during the reaction (Hoover and Hoover 1950: 242; Sisco and Smith 1951: 114). The latter operation helps the diffusion of gold and

silver from the ore phases to the lead bullion and the formation of lead oxide-rich slag, which contains the gangue components. After cooling, the slag attached to the resulting lead-rich bullion is removed from it and the bullion is placed in a hot cupel (Hoover and Hoover 1950: 242; Sisco and Smith 1951: 114). Upon heating, the lead is oxidised and most of the lead oxide is absorbed by capillary action into the porous texture of the cupel, while some of it is vaporised. When all the lead has oxidised, a bead of gold, silver or an alloy of both – depending on the ore assayed – settles in the top depression of the cupel. The cupellation is based on the difference in physical and chemical properties of lead oxide – litharge – and noble metals. If any other base metals are present, the litharge fosters their oxidation and forms with them fusible compounds with lower surface tension than that of noble metals. The lead oxide-rich phase wets the cupel and is hence absorbed, while the non-oxidised metals, i.e. gold and silver, remain on the surface as a small bead. When the cupel has cooled, the bead is weighed accurately to determine the quantity of precious metal held in the ore sample and therefore the proportion of these metals in the deposit.

This two-step process can be applied to gold and silver ores, both refractory and non-refractory (Hoover and Hoover 1950: 242, 244; Sisco and Smith 1951: 37-40). In the case of refractory ores, a preliminary oxidising step would be necessary, which would be the equivalent to large-scale roasting (see below). None of the sixteenth-century texts precisely explain how to roast an ore on a small scale in terms of reaction vessels to use, duration or temperature of the operation, or changing appearance of the ore to be observed in order to empirically follow the reaction, as usually written for large-scale roasting. Only Ercker briefly mentions that, in the case of silver ores, this small-scale roasting should be done as a separate operation by heating the ore on its own in a scorifier and study the state of the fumes released by the heated charge (Sisco and Smith 1951: 39). Further according to him, the two stages of roasting and scorification can be conducted in the same scorifier when working with silver-rich ores, by carefully regulating the temperature in the furnace; the temperature should be kept low at the beginning of the reaction to allow the ore to burn on top of the lead, and increased when the slag starts to form to begin the scorification itself (Sisco and Smith 1951: 38-39).

4.2.2.2. Second method: crucible fusion, scorification and cupellation

This second method starts with the reducing fusion of an ore in a triangular crucible, before scorification and finally cupellation. Refractory ores, similarly to the first sequence, would probably need to be initially oxidised – roasted – in a scorifier (Hoover and Hoover 1950: 242; Sisco and Smith 1951: 114). If the ore is not self-fluxing, i.e. its minerals are not readily fusible at the temperatures achieved in the furnace, fluxes can be added to the charge in the crucible (Hoover and Hoover 1950: 243; Sisco and Smith 1951: 112-114). When the flux(es) and the ore have melted, pure lead is added. Molten lead collects any gold and/or silver present and gathers at the bottom of the crucible, while a lighter layer of slag forms on top of it. The crucible is heated until it is believed that all the precious metals have been extracted from the ore, and then left to cool (Hoover and Hoover 1950: 243; Sisco and Smith 1951: 112). The crucible is then broken and the metallic layer or bullion, called *regulus* by Ercker (Sisco and Smith 1951: 112), and the slag are taken out. According to Ercker, both the lead bullion and the slag are scorified together (Sisco and Smith 1951: 112), whereas Agricola only recommends to further refine the bullion (Hoover and Hoover 1950: 243). This oxidation stage leads to the formation of a new litharge-rich slag together with a molten metallic phase, called “work lead” (Sisco and Smith 1951: 112), which contains a reduced amount of lead and the wanted metals. The main aim of the scorification would be to concentrate the noble metals. After cooling, the lead-rich bullion is separated from the slag and cupelled. The metallic button of noble metals resulting from the cupellation is weighed, giving the combined concentration in weight of gold and silver in the sample assayed.

The description of this second assaying technique by Agricola includes an “iron hoop” positioned in front of the bellows and filled with charcoal, on which the crucible is placed (Hoover and Hoover 1950: 226-7, 241), instead of a typical muffle furnace (Fig. 4.7). He also explains that ore or metal fusion in the crucible can be accelerated by introducing burning charcoals within the crucible and thus increasing the heat in the reaction vessel (Hoover and Hoover 1950: 241).

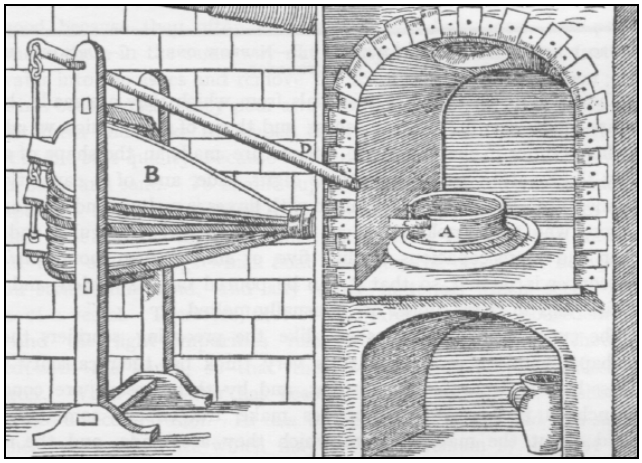


Fig. 4.7. *Iron hoop in front of bellows for crucible fusion (after Hoover and Hoover 1950: 227).*

After the fire assay, the bead of gold and silver is further refined by separating the two noble metals, an operation commonly called parting. This can be done following various techniques, such as cementation; parting with sulphur, antimony sulphide – stibnite – or, from the late Middle Ages onwards, mineral acids – this latter process being called inquartation (Hoover and Hoover 1950: 439-462; Sisco and Smith 1951: 162-201; Smith and Gnudi 1990: 188-205). The gold recovered from this final operation is weighed, giving the precise quantity of gold in the ore sample, the amount of silver being calculated by subtracting the weight of this gold bead from that of the cupelled gold-silver button. As previously explained, these various parting techniques will not be detailed here as the focus of this research is placed on the high-temperature metallurgical reactions.

4.2.3. Fluxes and collectors

As shown above, with very few exceptions, the collector universally recommended in fire assay for gold and silver is pure lead metal, because of its strong affinity with noble metals, and probably its availability and low cost. This lead needs to be free of any other metal to avoid the contamination of the assay, especially when assaying for silver, as lead and silver often occur together. If silver-free lead is not available, the lead has to be assayed separately to determine its silver content, before assaying the ore, metal or alloy to be tested. This control of the purity of the lead by the assayer is strongly advised by all three sixteenth-century authors (Hoover and Hoover 1950: 239; Sisco and Smith 1951: 45-46; Smith and Gnudi 1990: 139).

The description of the fluxes to add to the charge, when necessary, can be more ambiguous. For instance, Biringuccio unclearly refers to his fluxes for assaying ores as "whatever you have found goes with it best" (Smith and Gnudi 1990: 140). The criteria for choosing such specific fluxes apparently lie in experiments to be carried out by the assayer himself (Smith and Gnudi 1990: 143), as no precise guidelines or typical examples are provided in Biringuccio's text, rather an apparently random list of potential materials which could be used as fluxes.

Similarly, when Agricola refers to fluxes, he uses the Latin word "*additamenta*" which is translated as 'flux' by Hoover and Hoover. Although a flux is nowadays defined as a substance which lowers the melting temperature of the charge, Agricola's 'flux' includes the above definition as well as chemical reagents which can reduce, oxidise, sulphurise, desulphurise and collect materials of the charge (Hoover and Hoover 1950: 232). He also calls fluxes "those things which can liquefy it [the ore] and purge it of its dross" (Hoover and Hoover 1950: 241), therefore remaining vague on what compounds to add when one looks at the many recipes he gives, and leaving the choice to the assayer while conducting his experiment. He lists many compounds which can be used as fluxes, and several of which are reported below, and classifies them into four distinct categories (Hoover and Hoover 1950: 232-234). The selection of one or more fluxes for one particular assay seems to depend on the material(s) contained in the ore and on the fumes exhaled by the ore when heated (Hoover and Hoover 1950: 235-236). In the case of gold ores, Agricola also advises in various situations – even if not detailing which ones – the use of *sal artificiosus* or *sal torrefactus*, which are not readily understandable by the modern scholar; of "some powder compound which melts ore"; of glass-gall, which can be defined as a "neutral salt skimmed off the surface of melted glass" (Smith and Forbes 1969: 62; Tanimoto and Rehren 2008); or of roasted argol, a crude potassium hydrogen tartrate (Hoover and Hoover 1950: 242-243).

On the contrary, Ercker gives very precise recipes, which he uses to assay gold and silver ores. For gold ores, he produces his flux by mixing and melting litharge with antimony sulphide. Metallic iron in the form of filings is then to be added if the ore does not contain any iron, so that the sulphides combine with iron while gold and silver form an alloy with the antimony and the lead (Sisco and Smith 1951: 114), which then act as collectors for these precious metals. Although he does not acknowledge this, part of the silver could however also go into the sulphide-rich

layer due to the affinity of silver for sulphur. In the case of rich and clean gold concentrates, he also recommends a flux made of burnt argol and saltpetre (potassium nitrate) (Sisco and Smith 1951: 108-110). For silver ores, and particularly the refractory ones, he uses a "glass of lead", which is mostly composed of lead silicates (Sisco and Smith 1951: 33-34). More details about these fluxes are given below in the context of smelting.

Other fluxes are given for the crucible fusion of particular ores or specific situations in assaying, such as the presence/absence of an element in the ore or the refractoriness of the ore, among the main parameters influencing the selection of appropriate fluxes. Some examples are salt, vitriol (iron sulphate, copper sulphate), sal ammoniac (ammonium chloride), alkali carbonates (potassium and sodium carbonates), borax, crushed glass, pebbles, slag from previous smelting, metals (iron, copper), sulphides (pyrite, galena), etc.

A last important point to be made here is that, despite the relatively confusing depiction of the various fluxes and recipes, the proportion of reagents to be added are accurately quantified for each 'recipe'. The justifications for these particular ratios are not explained, and may simply be a reflection of the author's own experience – in the case of Biringuccio or Ercker, or observation – for Agricola.

The sixteenth-century treatises explain how to prepare the equipment needed for fire assay, how and when to combine the various collectors and fluxes and in which quantity, and finally how to conduct this operation. These written recipes are of higher interest if they find their equivalent in practice and this was where the scientific study of the assemblage from the Oberstockstall laboratory became relevant. As will be seen in chapter 5 of this thesis, this material has helped understand the practical side of fire assay in a particular context.

The metallurgical large-scale counterpart to fire assay being smelting, the following section will focus on industrial scale processes as described in the three written sources introduced above.

4.3. Large scale methods for smelting gold ores

If the fire assay of a specific geological deposit gives satisfactory results, it can then be subjected to extensive exploitation. The main steps to extract the metal include mining and smelting. Description of mining techniques has deliberately not been presented here and the emphasis has been placed on the smelting stage with only a brief introduction to the preparation of the ore before smelting, as the contemporary archaeological site of the Angertal, to which the texts have been compared, has provided material for the latter technology. The preparation for smelting, or beneficiation, of the ore extracted from the mine seems to be a crucial step for all three authors; a brief summary of the sixteenth-century depictions of the techniques used in beneficiation is therefore given first. Several aspects of this intermediate preparatory step may be of interest when interpreting the results from the scientific study of the archaeological assemblage from the Angertal.

4.3.1. The beneficiation of gold ores

Once gold ores have been mined from mineral veins or placers, or gold-rich sands have been taken out of the stream in which they accumulated, they need to be as clean as possible before being actually smelted. This operation is called the beneficiation of the ore; it allows the separation of the unwanted minerals, the gangue, from the worthy and sought after metal-rich minerals. There are various ways to beneficiate the ore but, as can be seen below, the choice of method usually depends on the type of mineral(s).

According to Agricola, Biringuccio, and Ercker, there seem to be three, sometimes four, successive steps to beneficiate gold from its deposits: a preliminary crude selection of relevant mineral-rich pieces, the crushing and grinding of these fragments and the washing of the resulting powder in order to concentrate it before smelting. The secondary gold deposited in rivers only requires washing and the application of amalgamation with mercury to the clean concentrates, the latter not being detailed here. For refractory ores, similarly to the operation performed on a smaller scale in scorifiers, an additional roasting of the gold-rich minerals may be required before pounding them (Hoover and Hoover 1950: 273-279; Smith and Gnudi 1990: 44, 137, 141-142).

4.3.1.1. Selection of material for future smelting

When the exploited ore is a vein, the gold-rich fragments need to be extracted from their host rock. In some cases, the crushing and sorting of the metal-rich minerals or gold fragments from their gangue can be carried out by hand (Hoover and Hoover 1950: 268-272; Sisco and Smith 1951: 101; Smith and Gnudi 1990: 14). The materials sorted by their estimated gold content can then be crushed, washed and potentially smelted separately, in order to limit the loss of precious metals in the slag if it is in too small quantities in the ore (Hoover and Hoover 1950: 268-270).

When sorting by visual examination is not feasible due to the complex nature of the mineralisation, the ore is entirely and directly crushed with various types of water-powered machines using wet or dry iron-headed stamps on a mortar (Hoover and Hoover 1950: 270-287; Sisco and Smith 1951: 101-102; Smith and Gnudi 1990: 44) and finely ground with water- or man-powered millstones (Hoover and Hoover 1950: 294-295) (Fig. 4.8). Agricola specifies that gold ore can actually be very finely crushed with a wet stamping mill (Hoover and Hoover 1950: 312-313). The three authors differ in their presentation of the methods, as Biringuccio and Ercker focus mainly on the principles and processes, generally not going into details about the tools, whereas Agricola also insists on the devices and equipments, giving very precise descriptions of the practical instruments used.

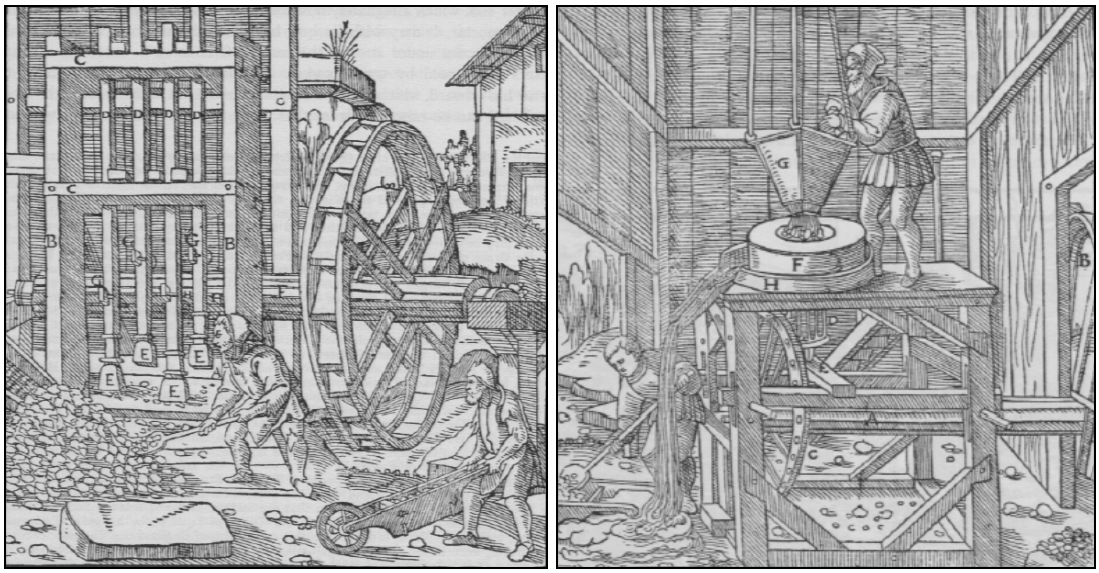


Fig. 4.8. *Drawings made from the descriptions of a stamping mill (left) and grinding stone (right) by Agricola (after Hoover and Hoover 1950: 284, 294).*

All types of ore, ground or not, need to be subsequently washed. This can be achieved using wooden boards called sluices on which water flows, boat-shaped wooden bowls called bateas, or trays put directly in the river or in troughs for sandy sediments (Hoover and Hoover 1950: 300-310; Sisco and Smith 1951: 97-100; Smith and Gnudi 1990: 30-44) (Fig. 4.9). All these methods rely on the high difference in density between the valuable pieces of gold or metal-rich minerals and their unwanted gangue fragments.

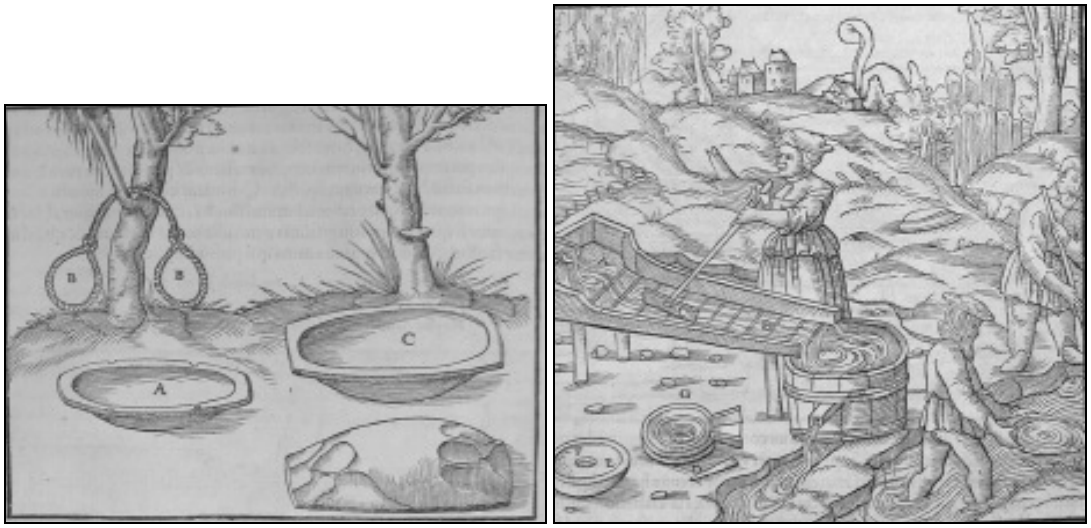


Fig. 4.9. *Representations of bateas (left) and sluices (right) by Agricola (after Hoover and Hoover 1950: 157, 326).*

In the case of refractory ores, before this whole sorting sequence, there may be a crucial and necessary step of roasting, which helps the grinding and smelting of the minerals afterwards.

4.3.1.2. Roasting

Roasting is a high temperature treatment under oxidising conditions, which physically and chemically alters the structure and composition of the ore to facilitate crushing, grinding, and its fusion during smelting operations.

“When their [the minerals’] facility of melting is brought near the dry hardness of the ores, as intermediaries they make them change their natures and dispose them to be better than they were before; and they make the dry and hard ores soft and tender” (Smith and Gnudi 1990: 143). With this statement, Biringuccio means that, on the one hand, roasting the ore softens the rock by removing loosely bound molecules; and, when followed by quenching in water, it physically cracks the

structure of the ore, inducing an easier grinding of a more brittle rock. Ercker recommends a similar roasting-quenching sequence and mentions that it would be helpful in the case of auriferous quartz or hornstones (Sisco and Smith 1951: 101-102). On the other hand, this operation may be applied to chemically prepare the ore for smelting, as it would partly oxidise it and drive off sulphur dioxide in the case of sulphides, or water and carbon dioxide in the case of carbonates. This leaves the structure porous enough to allow the reduction of the oxides into metal during the smelting. Besides, roasting chemically reduces the amount of undesired gas species in the furnace. Such a process would therefore be useful for the processing of auriferous pyrites.

Biringuccio recommends roasting to be performed in a reverberatory furnace, which heats the ore by radiation of the flames on the roof of the furnace, and not in a blast furnace where he believes the fire is too strong (Smith and Gnudi 1990: 144), while Ercker (1574) describes roasting furnaces as rectangular open-shaft brick structures, working with natural draught and in which the ore is placed on top of a pile of wood (Sisco and Smith 1951: 102-3) (Fig. 4.10). Wood fire is also cited by Agricola, who advises to roast the ore in open piles (Hoover and Hoover 1950: 273-274) (Fig. 4.11) except in the case of sulphur-rich minerals, which, according to him, should be roasted in a vaulted furnace. The latter technique uses pots filled with cold water, into which the vapours of sulphur released by the heated minerals are dissolved and collected (Hoover and Hoover 1950: 276-279).

Fig. 4.10. *Roasting furnace by Ercker (after Sisco and Smith 1951: 104).*

Fig. 4.11. *Examples of roasting hearths from Agricola's book (after Hoover and Hoover 1950: 277).*

4.3.2. The smelting of gold-bearing ores

All written sources stress that smelting is essential after the beneficiation to either remove more gangue impurities from selected metal-rich concentrates – especially in the case of gold –, or extract the metal to liberate it from the minerals in which it is trapped (Hoover and Hoover 1950: 353; Smith and Gnudi 1990: 141,

145). The smelting of gold ores is usually carried out on a large scale in blast furnaces, which allow the strong fire required for such an operation, although Biringuccio appears to have seen or heard of the use of natural draught and reverberatory furnaces for smelting operations (Smith and Gnudi 1990: 145-152) (Fig. 4.12). Agricola describes the building and operating of smelting furnaces in great detail (Hoover and Hoover 1950: 353-391). Ercker describes the use of blast furnaces for the smelting of copper ores (liquation process), and lead and iron ores (Sisco and Smith 1951: 250-253, 266-273, 288), but not for gold or silver ores. He explains that gold-rich ore fragments are to be melted in a crucible in a wind-furnace (Sisco and Smith 1951: 108-109), which surely limits the quantity of ore to be processed at the same time and would probably not be suitable for an industrial production. For small quantities of ores to be processed, Agricola also describes the smelting of gold ores with fluxes in a crucible in a similar furnace working with natural draught (Hoover and Hoover 1950: 396-398).

Fig. 4.12. *Representations of blast furnaces from* De Re Metallica *(left, after Hoover and Hoover 1950: 387) and a reverberatory furnace as described in* The Pirotechnia *(right, after Smith and Gnudi 1990: 151).*

4.3.2.1. Brief technical description of blast furnaces

Blast furnaces were adapted from the iron metallurgy of the medieval period and down-sized, being generally 0.8 meter wide and 2 meter high during the Renaissance (Tylecote 1976: 93). They are usually composed of a shaft, a hearth, a forehearth in

front of it and sometimes a complementary dipping-pot or ditch. The walls are usually made of soft refractory stone and sometimes of bricks for the front wall (Hoover and Hoover 1950: 355) with a renewable lining of clay. Tuyères are inserted in holes in the furnace walls, to which the nozzles of water-powered bellows are connected in order to ensure the air supply (Hoover and Hoover 1950: 355-356, 362; Smith and Gnudi 1990: 148) (Fig. 4.13). The blast furnaces described by Biringuccio, Agricola and Ercker all work following the same principle, they only differ in some construction details and shapes. Biringuccio's furnaces are mill hopper-shaped, wide at the mouth and narrow at the bottom (Smith and Gnudi 1990: 145-50) (Fig. 4.14), while Agricola's and Ercker's descriptions show rectangular shafts (Hoover and Hoover 1950: 355-65; Sisco and Smith 1951: 236,274) (Fig. 4.15).

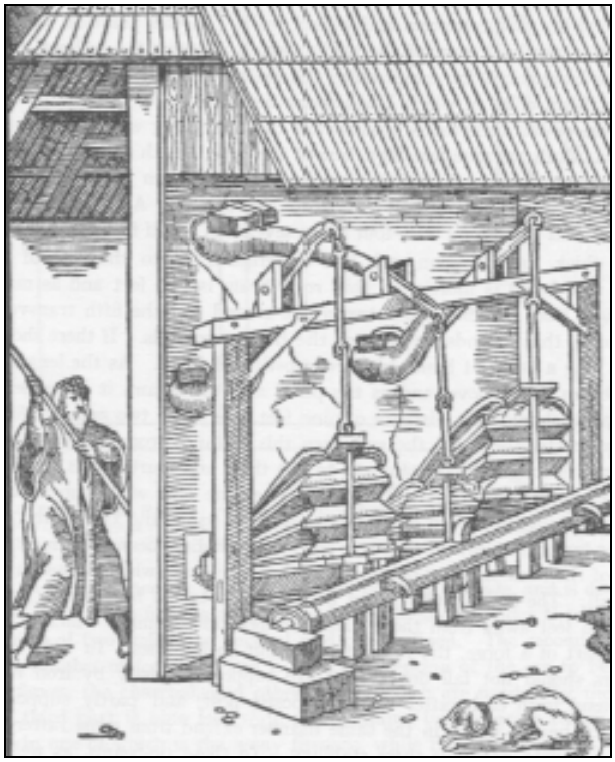


Fig. 4.13. *Bellows connected to the back wall of blast furnaces (after Hoover and Hoover 1950: 359).*

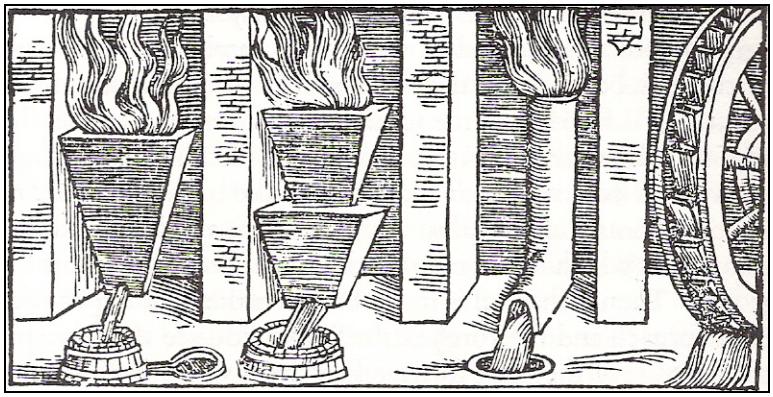


Fig. 4.14. *Blast furnaces by Biringuccio (after Smith and Gnudi 1990: 150).*

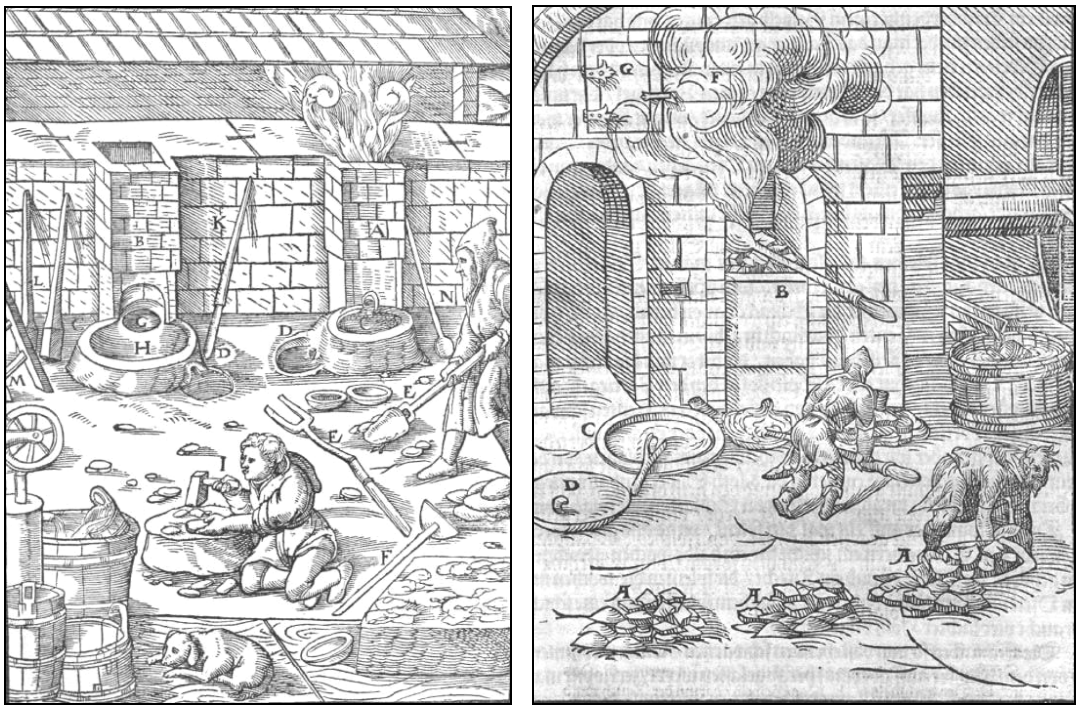


Fig. 4.15. *Examples of blast smelting furnaces depicted by Agricola (left, after Hoover and Hoover 1950: 387) and by Ercker, the latter apparently only used in the case of the smelting of copper and lead ores (right, after Sisco and Smith 1951: 236).*

4.3.2.2. Depictions of smelting procedures

Leaving Ercker's method aside, according to Agricola and Biringuccio, the smelting methods generally used in the case of gold ores are relatively similar. The smelting activity is described by Agricola to be usually carried out by two craftsmen: the master and his assistant. The smelting process starts with the pre-heating of the furnace – hearth and forehearth – and the introduction of the charge from the top in the hot furnace, this charge being composed of ore(s), fluxes, and a collector, the latter being particularly essential in the case of precious metals. This charge is then melted and, when considered to have reacted enough, or when the furnace is full, the

whole melt is tapped out by the smelter through a hole made in the front wall of the furnace into a forehearth, with first the slag, then the matte and finally the lead bullion successively flowing out of the furnace (Hoover and Hoover 1950: 379-382; Smith and Gnudi 1990: 153-155). This molten substance subsequently further separates into three distinct layers upon cooling in the forehearth: slag at the top, matte in the middle and lead bullion at the bottom (Hoover and Hoover 1950: 381; Smith and Gnudi 1990: 153-154). The tapping of the melt apparently taking place consecutively for each phase, starting with the slag, sounds relatively confusing, for there only seems to be one tapping hole in the descriptions of blast furnaces, through which all layers would go through: one may therefore wonder how the smelter could ensure the slag to flow out first. Besides, bullion and matte have a higher density and a lower viscosity than slag (Vaisburd and Brandon 1997), therefore if the hole is at a relatively low height, which would be expected in order to be able to transfer all the charge into the forehearth, then metal would arrive first followed by matte and then slag. This counter-intuitive description does most likely not represent the actual practice of tapping.

When all the charge has been transferred into the forehearth, the front wall hole is then closed and the furnace filled again. Agricola explains that the slag, the sulphur-rich material, which he calls “pyrites”, and the gold-silver-lead “alloy” should be tapped out in a hot forehearth, in which lead metal has been previously melted (Hoover and Hoover 1950: 381). This additional lead metal would ensure a sufficient overall quantity of lead to capture all the gold. The solidifying slag and matte are sequentially skimmed off the surface of the lead pool with an iron implement. On the one hand, according to Agricola, the lead bullion produced within the furnace from the smelting should be taken out of the forehearth only once all the ore selected for the day has been smelted (Hoover and Hoover 1950: 382). On the other hand, Biringuccio has the molten lead further poured into a ditch attached to the forehearth (Smith and Gnudi 1990: 154). According to Agricola, variations in the process only lie in the use of the tap-hole, as it can be opened intermittently or always kept open, in which latter case dipping pots are to be added to the side of the forehearth. This would lead to a relatively similar situation to Biringuccio’s, for which the lead bullion containing the precious metals is poured in these dipping-pots, one major difference being that Agricola advises to pour the “pyrites” in these as well, before turning them into cakes, breaking these cakes and throwing them

back in the furnace (Hoover and Hoover 1950: 386). In the case of refractory gold and silver ores, however, he recommends to open the tap-hole intermittently, i.e. to have it closed initially in order to allow all the components of the charge to melt and react together before being poured out of the furnace into the forehearth (Hoover and Hoover 1950: 383-384).

The lead bullion is finally taken out of the forehearth and saved for further cupellation and parting operations, to recover the gold and silver at the end of the whole technical sequence. Agricola also advises to keep every type of waste materials produced by the smelting and divide them following their richness in gold for future re-melting in a furnace with lead and appropriate fluxes (Hoover and Hoover 1950: 381-382). Biringuccio explains the re-processing of copper-rich sulphidic material, through liquation, to separate copper from the precious metal (Smith and Gnudi 1990: 156-158).

4.3.2.3. Fluxes and collectors

Although there seems to be a large variety of methods and charge compositions suggested by the Renaissance treatises for smelting gold-rich ores, they are all based on similar chemical principles. Following Agricola's explanation for the processing of large quantities of minerals, a definite proportion of ore, lead, sulphur-rich materials – also called "pyrites" – and other appropriate fluxes, charcoal and slag are introduced and melted together in the blast furnace (Hoover and Hoover 1950: 379). Biringuccio adds layers of equal proportions of galena and slag to the ore (Smith and Gnudi 1990: 153). A wider range of procedures is presented by Agricola when smelting smaller quantities of gold ores in a crucible, adding fluxes as different as lead, litharge, "hearth-lead" – the bottom of cupellation furnaces saturated with lead oxide –, antimony sulphide, sulphur, silver, slag, copper, iron, glass-gall, argol, salt, or saltpetre, which are generally similar to those used for the fire assay of gold ores (Hoover and Hoover 1950: 396-398) (see above).

During smelting, lead, silver and antimony would be reduced, when not already in their metallic state, and act as collector for gold (and silver when present). In both the furnace and the crucible, the use of sulphur would help the formation of a matte layer, into which copper and part of the silver would preferentially go. A lead bullion richer in gold, containing less impurities, and more easily cupelled, could therefore

be produced. When working on a large scale, Agricola advises in most cases to roast and re-melt the matte layer (Hoover and Hoover 1950: 399), which would allow the smelter to recover most silver.

Iron may be added to the charge as iron metal (filings), oxide (scales) or both, and reacts with sulphur to form some matte and/or with silica – often present as gangue for gold ores – to help the melting of the charge and the formation of fayalitic slag. To further promote the formation of fayalitic slag, iron slag or slag of other smelted ores are added to the charge.

While Agricola apparently lists no fewer than eighteen recipes for his fluxes (Smith and Forbes 1969: 63) and in particular eight for smelting gold ores on a small scale (Hoover and Hoover 1950: 396-398), Ercker seems to only use two. His first flux is the so-called "black flux", and is made by crushing saltpetre and argol, mixing them together in a 1:2 ratio, then burning the mixture in a lidded crucible and finally mixing the resulting product with some salt, glass-gall and argol (Sisco and Smith 1951: 110). The chemical reactions involved would mainly produce potassium nitrite, potassium carbonate and carbon (Smith and Forbes 1969: 63). Ercker's second flux is called "glass of lead", and is a lead silicate glass, which is produced by melting litharge, crushed and fused pebble stones, and salt together in a well-sealed crucible (Sisco and Smith 1951: 34). However, in the case of gold concentrates and absence of mercury for amalgamation, Ercker uses a flux made of glass-gall mixed with *caput mortuum*, the latter being the residue resulting from the distillation of parting acid and which would be mostly composed of ferric oxide and potassium sulphate (Smith and Forbes 1969: 63). As mentioned before, Ercker's methods and fluxes are however explained only on the small scale of crucible fusion.

4.4. Summary

This chapter has explained the procedures and equipment used in small-scale fire assay and in large-scale smelting operations of gold ores according to three major sixteenth-century texts, which would remain fundamental to metallurgical technologies for several centuries. These technical descriptions generally follow similar chemical reactions and principles but can initially appear confusing given the wide variety of recipes and methods presented, which involve a large number of reagents and sometimes distinct sequences from one book to another.

These depictions were fully incorporated in this research and used as a means of comparison with the representations of their actual practice, found in the assemblages of the laboratory of Oberstockstall and of the gold smelting site of the Angertal. The later chapters dedicated to the study of these two archaeological sites will show that, on the one hand, most of the procedures documented archaeologically match their contemporary descriptions but that, on the other hand, some clear variations have been identified, especially in Oberstockstall. As will be argued later in this thesis, the results from this research have highlighted the value of comparing historical and archaeological sources in order to obtain as clear a picture of ancient technologies in their contexts as possible.

Chapter 5 -The remains from Oberstockstall: evidence for small-scale metallurgical activities

5.1. Introduction

The ceramic and glassware from the sixteenth-century site of Oberstockstall have very specific forms clearly pointing towards specialised laboratory instruments. Among the artefacts were found numerous vessels of several sizes used for distillation, assaying, small-scale melting and smelting, and further furnace equipment such as muffles (Fig. 5.1). This particular assemblage of alembics, glass phials, distillation columns and flasks, funnels, and assay furnace vessels and tools, suggests at first sight that both chemical and metallurgical activities were taking place. The material collected from both excavation seasons has been comprehensively catalogued and macroscopically described, and the instruments with the most diagnostic shapes have also been identified and classified by von Osten (1992; 1998), referring to contemporary written sources when necessary.

Fig. 5.1. *Various ceramic and glass apparatus from Oberstockstall, diagnostic of a laboratory (after Martinón-Torres* et al. *2003; scale bar 15 cm).*

Ceramics constitute the major component of this assemblage, mainly triangular crucibles, cupels and scorifiers (Fig. 5.2) as well as a significant number of larger and more ordinary pots. The three former types of technical ceramics were used in high-temperature operations, which are the main focus of this project: many of them show characteristic residues of use, such as crystalline salts, metallic drops and slag layers; and traces of burning from the fire. The description, characterisation, and analysis of the triangular

crucibles, scorifiers and bone-ash cupels have been comprehensively carried out (Rehren 1998; Martinón-Torres *et al.* 2003; Martinón-Torres and Rehren 2005; Martinón-Torres and Rehren 2009), mainly as part of a completed PhD project (Martinón-Torres 2005: 100-171). Based on these previous studies, only a brief description of these particular technical ceramics is given here, since the current project aims at the determination of their utilisation.

5.1.1. The crucibles

Crucibles can be of various shapes, fabrics and sizes and were used worldwide in the past for a variety of high-temperature processes, many related to metals, such as melting, smelting, cementation (Bayley 1991; Bayley 2001), brass-making (Bayley 1984; Rehren 1999) or the production of crucible steel (Rehren and Papachristou 2003), but also to other materials, such as glass (Rehren 1997; Bayley 2000). The variability of these vessels promoted a classification based on their typology and functionality, which showed that, despite a very wide range of utilisations, their technical features could allow these artefacts to be used as both functional and cultural indicators (Rehren 2003; Bayley and Rehren 2007). Within the framework of this particular research, despite very diagnostic technical attributes, their versatility however induced a need for a more precise definition. For the purpose of this thesis, crucibles will be defined as "free standing, movable vessels, used for 'dry', that is high-temperature, metallurgical operations" (Rehren 2003: 207; Bayley and Rehren 2007).

As already seen in the previous chapter (cf. chapter 4), the name of the triangular crucibles is drawn from their diagnostic shape (Fig. 5.2 and Fig. 4.4, p. 91), and the triangular crucibles from Oberstockstall (Fig. 5.3) perfectly match their written description. They are made of rather refractory clay, usually with graphite inclusions, allowing them to withstand heat and chemical reactions, such as aggressive attacks by molten metal oxides and fluxes. Though their overall shape is the same throughout the assemblage, their sizes can vary considerably, from *ca.* 1.5 to 18.5 cm high (Martinón-Torres 2005: 104-117; Martinón-Torres and Rehren 2005).

The scorifiers of Oberstockstall are shallow thin-walled vessels manufactured with either graphitic or quartz-rich clay (Fig. 5.4). In a similar way to the triangular crucibles, their appearance is very close to the depiction of such vessels given by

Ercker and Agricola (cf. chapter 4). Their fabric mainly consists of two types, the first being graphitic and similar to that of the triangular crucibles and the second rich in quartz inclusions (Martinón-Torres 2005: 143-144). The latter allows for reactions to take place between the ceramic and the oxidising charge. Two morphological types of scorifiers can be distinguished in Oberstockstall, one having a thicker base and a smaller diameter than the other. Their sizes range between *ca*. 5.5 and 20 cm for the rim diameter and 2-3 cm for the height (Martinón-Torres 2005: 141-159). The shape of the scorifiers already indicates that they could have been used for oxidising reactions, perhaps within an assaying sequence. However, as with the crucibles, their functional adaptability to various utilisations – and the restricted documentary explanation of the use of both types of reaction vessels – means that a more detailed investigation is required in order to understand their specific use in this laboratory. It is expected that the study of the Oberstockstall material will shed more light on the specific uses of these vessels.

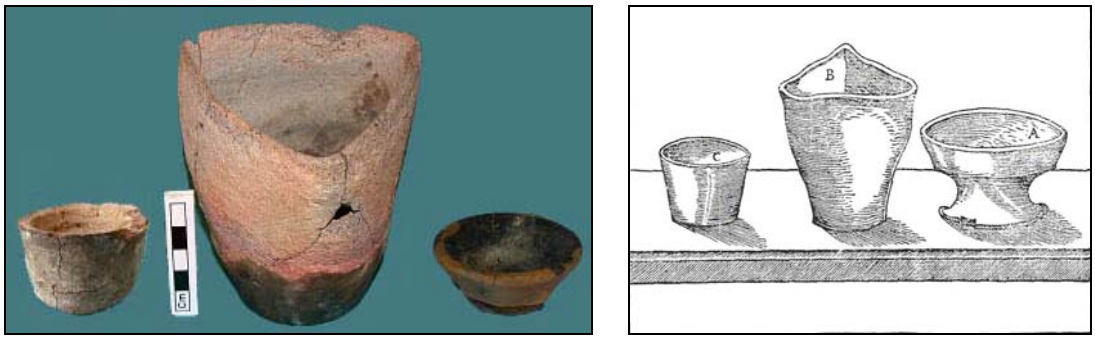


Fig. 5.2. *From left to right: cupel, triangular crucible and scorifier from Oberstockstall (left; scale bar 5 cm; photo: M. Martinón-Torres) and as depicted by Agricola (right, after Hoover and Hoover 1950: 229).*

Fig. 5.3. *Two large graphitic triangular crucibles (left, scale bar 5 cm) and a selection of small used and unused triangular crucibles (right, scale bar 3 cm) from Oberstockstall (photos: M. Martinón-Torres).*

Fig. 5.4. *Scorifiers from Oberstockstall (after Martinón-Torres 2005: 141; scale bar 15 cm).*

As briefly explained before (cf. chapter 4), cupels are open dishes shaped as a truncated cone, with a very thick lower part, and usually made of finely ground wood or bone ash, at least since the late medieval period – earlier cupels were made of mixtures of clay marls, crushed shell and bone ash (Bayley and Eckstein 2006). Likewise, the cupels from Oberstockstall can clearly be identified when compared to the written sources (Fig. 5.5 and Fig. 4.4, p. 91). These are thick vessels composed of a porous body made of a finely crushed mixture of bone and wood ash (Martinón-Torres *et al.* 2009) – earlier studies had incorrectly identified clay instead of wood ash in the mixture with bone ash (Rehren 1998). These archaeological cupels show a shallow depression on the top surface covered with a layer of pure bone ash. These vessels were most likely used for cupellation as the last high-temperature operation of the sequence. The cupels from Oberstockstall have been classified in four size categories, from 1.5 to 4.5 cm high and with a diameter of 3 cm up to 10 cm (Martinón-Torres 2005: 160-171).

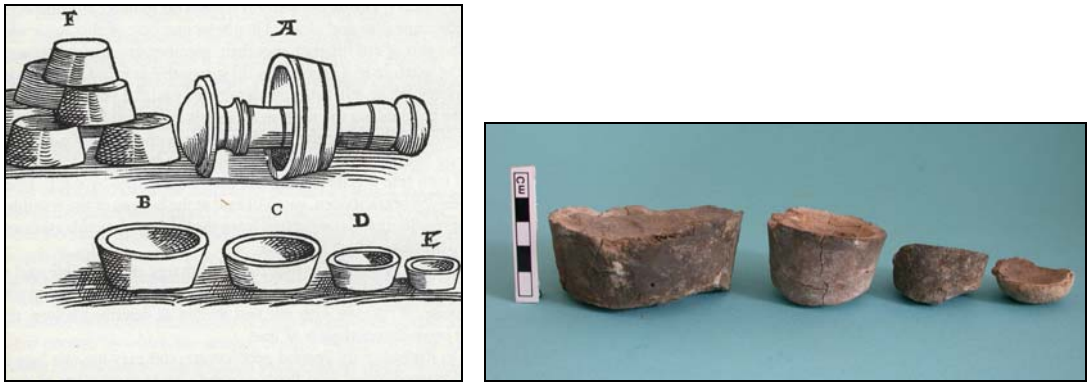


Fig. 5.5. *Cupels of different sizes with their moulds as depicted by Ercker (left, after Sisco and Smith 1951: 33), and cupels from Oberstockstall (right, after Martinón-Torres 2005: 162; scale bar 5 cm).*

5.1.2. Metallurgical residues

The high-temperature processing of raw materials in these vessels resulted in the formation of distinct products, part of which can still be found in the archaeological record. These chemical and metallurgical remains are mainly slag and matte, and occasionally metal, which has oxidised to a certain extent during burial. The study of these materials will help understand the specific utilisation of these various instruments and allow a reconstruction of the different processes and techniques used. Two types of products have been identified: on the one hand, residues still attached to used vessels, such as the characteristic black glassy layer that can be seen in some used crucibles, or the slag layer, presenting various colours, which covers used scorifiers (Fig. 5.6); on the other hand, fragments of slag, metal and matte probably produced in these vessels but later removed from them (Fig. 5.7).

Fig. 5.6. *Metallurgical residues within two scorifiers (scale bars 5 cm; photos: M. Martinón-Torres).*

Fig. 5.7. *Two morphologically different types of matte cakes: triangular (left) and circular (right) (scale bars 5 cm; photos: A. Mongiatti).*

A preliminary study involving a few analyses included several metallic pieces, ores, and a few cupels and scorifiers (Soukup and Von Osten 1991; Von Osten and Soukup 1992; Soukup and Von Osten 1992; Soukup and Mayer 1997; Von Osten 1998). Around nineteen pieces of various ores have been identified, revealing diverse sulphidic ores, such as pyrite, arsenopyrite, chalcopyrite, antimonite, tetrahedrite, and galena (Soukup and Mayer 1997: 64-65); in the sixteenth century, these ores were typically exploited for their gold and/or silver content.

However, more investigation was needed in order to get a clearer picture of the activities at this intriguing Renaissance laboratory. Therefore, sixteen waste products from crucibles and thirteen from scorifiers, as well as six cakes and fragments of matte, one piece of slag and three metalloid lumps were studied and analysed

following the methodology detailed in chapter 3, namely a combination of metallography and chemical and phase analysis mainly using SEM-EDS. This scientific study mostly focused on the remains formed in crucibles and scorifiers, as these were versatile tools whose function in the technical sequence(s) occurring in Oberstockstall or other contexts is difficult to attribute without analysing their residues. The analytical data of the remains within the bone- and wood-ash cupels are outlined to a smaller extent based on previous characterisation studies (Rehren 1998; Martinón-Torres and Rehren 2005; Martinón-Torres *et al.* 2009). Besides, these latter vessels have a more specialised purpose, namely cupellation, than the crucibles and scorifiers. The composition of their residue should relate to the composition of the bullion being tested. However, cupellation could be related to production, assaying or recycling (Bayley and Eckstein 1997). Thus, the results from their scientific study will be briefly summarised and discussed within the context of the activity of the laboratory in Oberstockstall.

This chapter presents the extensive description and analytical study of the various metallurgical remains briefly introduced above. It also includes references to major sixteenth-century written sources that contribute to the understanding of several high-temperature processes, in order to attempt the reconstruction of the techniques and procedures employed in Oberstockstall, and try to identify the purpose of these operations.

As will be shown in this chapter, the archaeometric and historical study provides a rather vivid picture of a laboratory where a variety of minerals were processed, probably to be tested for their noble metal content. Within the broad complexity of reactions identified, it is possible to define a main suite of operations that appears particularly conspicuous. This procedure started with the reducing fusion of a fahlore – probably containing some precious metal and having grown in a gangue of calcite and/or quartz and possibly associated with other base-metal sulphides – with lead added as a collector for the noble metals, and iron filings, salt(s) and glass used as fluxes. This first stage in the sequence would generate three separate products: a lead-rich bullion at the bottom of the crucible, a matte layer above it and a slag cover on top of all, showing a density-controlled succession of a metallic, a sulphidic and finally an oxidic siliceous phase. This stage was followed by the scorification of the lead bullion, the matte being also occasionally scorified and the slag discarded. The lead button, probably reduced in volume through several steps of scorification and

containing almost all of the noble metals, was finally cupelled in one of the ash cupels. Though this technical route appears to be the main *modus operandi* in Oberstockstall, some variations exist and will be discussed as well.

The characterisation of the various archaeological materials, namely the residues from the triangular crucibles, the scorifier remains, and the slag, matte and metallic fragments, is presented below. The discussion of the archaeometric data of this archaeological material details and substantiates the argument made here for this particular case study.

5.2. The residues in the triangular crucibles

5.2.1. Characterisation

All the triangular crucibles sampled show a graphite-rich ceramic fabric. Most of the samples analysed were removed from the upper rim of the vessels, generally as a cross-section of both the ceramic and the metallurgical residues from the upper area of the inner surface. These products, formed at high temperature inside the crucible, typically have a black and shiny appearance, usually both macroscopically and microscopically (Fig. 5.8). In the few cases where invasive sampling of the ceramic was not possible, residual particles were scraped from the surface inside the crucibles. These also appear shiny dark, but frequently with green areas characteristic of corrosion products of copper, similarly to the matte fragments. The various remains display a wide range of variation, from an apparently homogeneous glass to very heterogeneous phase mixtures (Fig. 5.9). Most of these pieces of slag, matte and oxidised metallic residues have very complex microstructures, except for a few of them which are composed of a very homogeneous matrix almost devoid of inclusions. This probably reflects variations in the practical and experimental conditions of the procedure, different steps in a sequence, or even the processing of diverse raw materials. However, it is possible to identify some common features in the crucible residues, most notably in the typical presence of lead, antimony, copper, iron and silver.

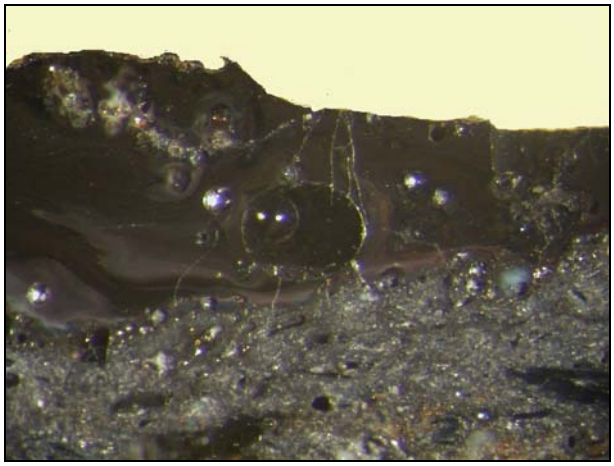


Fig. 5.8. *Black slag adhering to grey ceramic. Image from the stereomicroscope (OB 345/S1, 40x, long axis ~4 mm).*

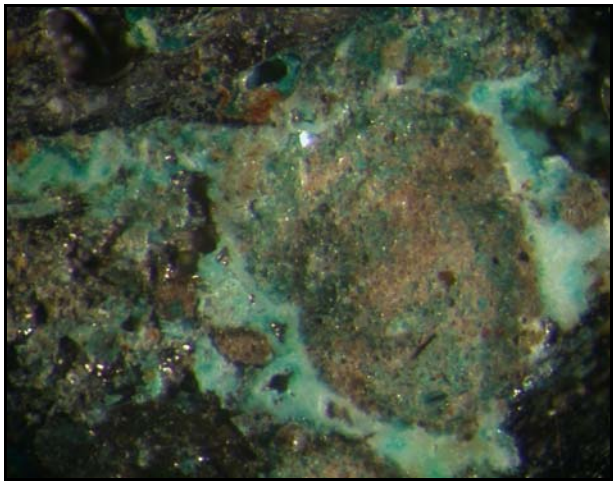


Fig. 5.9. *Very heterogeneous and corroded crucible residue. Image from the stereomicroscope (OB 307/S2, 40x, long axis ~4 mm).*

5.2.1.1. Slag phases

As can be seen in Table 5.1, the matrix of most of the crucible slag residues is mainly composed of a silica-rich glass, with SiO_2 ranging from 25 to 54 wt%, with an average of *ca.* 39 wt%. Besides silica and alumina, which varies between 4 and 18 wt% with an average of *ca.* 9 wt%, the glass phases show significant levels of the oxides of sodium (0.1 to 10 wt% Na_2O, average of *ca.* 5 wt%), potassium (2 to 7 wt% K_2O, average of *ca.* 4 wt%) and magnesium (0.1 to 2 wt% MgO, average of *ca.* 2 wt%). Calcium and iron oxides are also detected in high amounts, their concentrations varying respectively between 4 and 14 wt%, and 6 and 26 wt% (averages of 8 wt% CaO and 14 wt% FeO) (Table 5.1). Within this set of analysed specimens, three samples have unusually high concentrations of antimony oxide (OB 479/S1: 41 wt% Sb_2O_3, OB N001: 21 wt% (OB/N001/S1) and 12 wt% (OB N001/S2) Sb_2O_3) and one sample has an exceptionally high amount of lead oxide (OB 509/S1: 35 wt% PbO).

Most of these slag samples are relatively dense, exhibiting only a few fairly large pores (50 to 100 μm). However, porosity remains variable from sample to sample: for instance, OB 509/S1 has a specific orientation in lines of numerous small voids (up to 10 μm) within the glass, while OB 461/S1 has almost no inclusions but more pores than any of the other slag residues analysed.

The glass matrices of the crucible slag generally contain numerous phases of magnetite spinels, of different sizes depending on the samples but never larger than 30 μm. OB N003/S1 displays abundant primary phases of wüstite instead of newly grown crystals of magnetite. This, together with the formation of matte (see below), is indicative of the strongly reducing conditions of the process performed in the triangular crucibles. This is consistent with observations in the crucible fabrics, where most often graphite inclusions have not been burnt off (Martinón-Torres 2005: 134). Moreover, several triangular crucibles show evidence of having been used with lids and lute, which would facilitate the creation and control of such conditions within these reaction vessels (Martinón-Torres 2005: 118-119).

Several samples also display alkali-rich phases, such as potassium and/or sodium silicates (feldspathoids) (OB 307/S2, OB 461/S1, OB N003/S1) and the slag of OB 307/S2 exhibits crystals of fayalite (Fig. 5.10). The presence of these particular crystals, which formed in the melt separate from the glass, indicate a working temperature in the crucible furnace of around 1150 - 1250 °C, since this range of temperatures lies just above their crystallisation temperature. Their acicular shape and fairly small size further suggest a relatively fast cooling rate.

	Na_2O wt%	MgO wt%	Al_2O_3 wt%	SiO_2 wt%	P_2O_5 wt%	SO_3 wt%	Cl wt%	K_2O wt%	CaO wt%	TiO_2 wt%	MnO wt%	FeO wt%	CuO wt%	ZnO wt%	Sb_2O_3 wt%	PbO wt%
OB 307/S2	5.0	0.1	9.4	45.5	0.5	0.8	1.0	3.1	6.4	b.d.l.	b.d.l.	13.1	b.d.l.	7.8	0.5	6.8
OB 461/S1	9.8	1.7	18.4	53.5	0.1	0.6	1.1	2.7	4.1	1.4	b.d.l.	6.2	b.d.l.	0.4	b.d.l.	b.d.l.
OB 479/S1	6.1	1.3	5.5	28.0	b.d.l.	b.d.l.	1.1	6.8	3.5	0.9	b.d.l.	6.5	b.d.l.	b.d.l.	40.3	b.d.l.
OB 494/S1-2	4.3	2.1	12.7	38.9	1.3	0.3	0.4	4.2	13.0	0.5	b.d.l.	16.3	0.4	b.d.l.	5.6	b.d.l.
OB 498/S1	7.2	1.1	12.5	39.0	0.4	1.6	1.6	1.7	6.6	0.2	b.d.l.	18.4	b.d.l.	0.1	9.6	b.d.l.
OB 509/S1	4.1	1.7	5.5	35.9	0.3	b.d.l.	0.4	2.7	6.6	0.4	b.d.l.	7.7	b.d.l.	0.1	b.d.l.	34.6
OB N001/S1	0.1	1.9	3.8	25.3	2.0	0.5	b.d.l.	2.9	13.9	b.d.l.	b.d.l.	17.1	4.6	0.4	21.0	6.5
OB N001/S2	0.1	2.3	7.6	45.7	0.7	0.5	b.d.l.	4.7	6.1	b.d.l.	b.d.l.	14.5	4.2	0.1	12.0	1.5
OB N003/S1	9.7	1.4	8.2	34.9	0.5	4.5	0.7	2.6	10.2	1.2	b.d.l.	26.0	b.d.l.	0.1	b.d.l.	b.d.l.
OB S004/S1	7.1	1.1	2.9	50.2	0.7	2.6	0.9	6.6	1.0	2.4	0.8	23.7	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Average of ceramic matrices*	0.2	0.7	32.2	57.0	0.2	b.d.l.	b.d.l.	2.1	0.6	1.4	b.d.l.	5.6	b.d.l.	b.d.l.	b.d.l.	b.d.l.

***** after Martinón-Torres and Rehren 2005b

Table 5.1. *Average chemical composition by SEM-EDS, normalised to 100 wt%, of glass matrices of inner crucible slag residues and of the separate slag lump OB S004 (b.d.l.: below detection limit). See appendix 2 for the full results.*

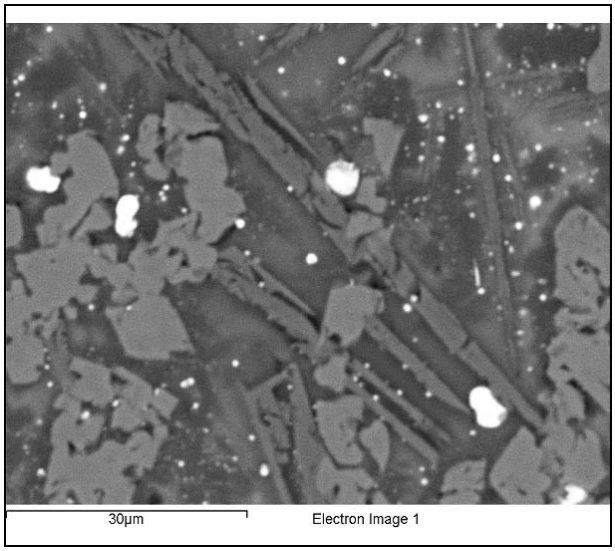


Fig. 5.10. *Slag composed of a dark grey glass; cubic light grey magnetite crystals; acicular light grey olivine crystals; and bright minute prills of lead, antimony and copper sulphide (OB 307/S2, BSE, 1600x).*

Most slag layers contain a diversity of matte inclusions and prills - either metallic or partially oxidised. This is due to the fact that, although three layers probably formed in the vessels (metal, matte and slag), these would not be completely and neatly separated. The matte inclusions are variously composed of iron sulphide (OB 345/S1, OB 461/S1, OB 494/S1, OB 494/S2, OB 498/S1), lead sulphide (OB 307/S2, OB 345/S1, OB N001/S2), antimony sulphide (OB 307/S2) and copper sulphide (OB 345/S1, OB 494/S1, OB 494/S2, OB 498/S1), and in some cases of a mixture of these sulphides (OB N003/S1). Prills of metallic antimony and copper,

sometimes associated with lead are found in three specimens (OB 494/S1, OB 494/S2, OB 498/S1); inclusions of antimony oxide are detected in five others (OB 307/S2, OB 345/S1, OB 494/S2, OB 498/S1, OB N001/S1) (Fig. 5.11).

It is also important to note that silver has been detected in the prills of several slag samples analysed (OB 461/S1, OB 494/S2, OB N001/S1), suggesting that precious metals were an important component of the metallurgical activity taking place at Oberstockstall.

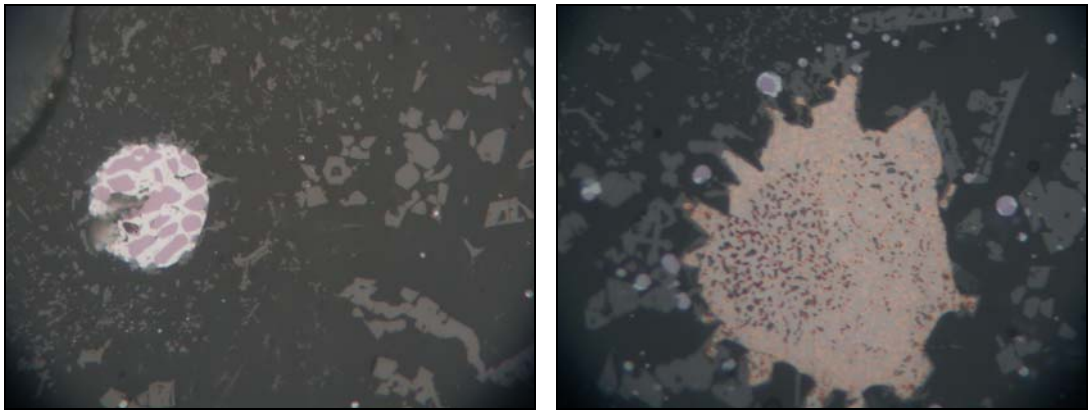


Fig. 5.11. *Examples of two metallic inclusions: a prill composed of a copper antimonide (Cu_2Sb, pink) and a solid solution of antimony and copper (white) (left); a bright orange prill of copper containing some antimony (right) (OB 494/S2, optical microscope, plane polarised light, 1000x, long axis ~150 μm).*

Only one free piece of slag, detached from its original ceramic vessel, has been found among the group of artefacts excavated from Oberstockstall. This slag is composed of two silicate phases: an iron-silicate glass, enriched in soda and potash mainly, containing crystals of a solid solution of composition similar to the mineral augite (53 wt% SiO_2, 22 wt% CaO, 13 wt% FeO, 9 wt% MgO, 1wt % Na_2O, 1 wt% TiO_2, 1 wt% MnO) (OB S004/S1, Table 5.1). Large phases of pyrrhotite and cubanite ($CuFe_2S_3$), as well as cubic crystals of magnetite can also be seen (Fig. 5.12). The sulphides have locally oxidised into iron oxide, with lead and antimony oxides being detected as well. This slag piece shows significantly lower levels of calcium oxide (1 wt% CaO) and alumina (3 wt% Al_2O_3) than the slag samples attached to crucibles; however it has sufficient similarities in its microstructure and chemical composition to that of the crucible slag samples studied – i.e. its enrichment in iron and alkali oxides, the existence of sulphidic inclusions and the recurrence of the elements lead, copper and antimony – confirming that it was most likely produced in one of the triangular crucibles.

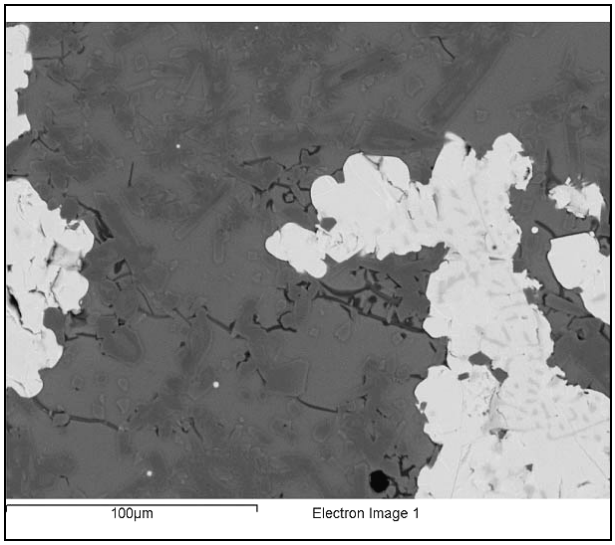


Fig. 5.12. *Slag composed of two pyroxene phases (medium grey and dark grey), and containing bright phases of iron-copper sulphides (OB S004/S1, BSE, 500x).*

5.2.1.2. Crucible bullion and matte

The various crucible residues analysed and identified as either slag, oxidised matte or bullion, only reflect the corresponding location within the crucible from where the samples were taken. However, as further discussed below, all three layers would have formed and be present in the crucibles used for reducing fusion. Crucible OB 307 is a good illustration of this, since scraping the surface of its inner walls in different areas uncovered the three types of residues: oxidised bullion for OB 307/S1; slag and matte for OB 307/S2.

The cross-section of OB 519B shows a matte layer attached to the ceramic, distinguished from the slag remains by its optically visible lustre. Like the matte fragments (discussed below), it is composed of a main sulphidic system with relatively large magnetite crystals and inclusions of antimony (95 wt% Sb), containing also some copper (2 wt%) and bismuth (2 wt%). The main sulphide phase consists of dendrites of tetrahedrite ($(Cu,Fe)_{12}Sb_4S_{13}$), similar to the phase noticed in the triangular matte cake (see below). Some primary phases of lead sulphide, now oxidised into sulphates, can also be noticed (Fig. 5.13). This particular sample, with matte still attached to a crucible wall, confirms the formation of a distinct matte layer during the reducing fusion of the ore in the crucible. It also attests to the metals constituting the ore, mainly antimony and copper, and may give information about the ore mineral itself, since this tetrahedrite phase could represent the original ore, which would have melted and recrystallised during cooling forming well-grown

dendrites. This is consistent with the identification of tetrahedrite in the ore assemblage found in the laboratory (Soukup and Mayer 1997: 64).

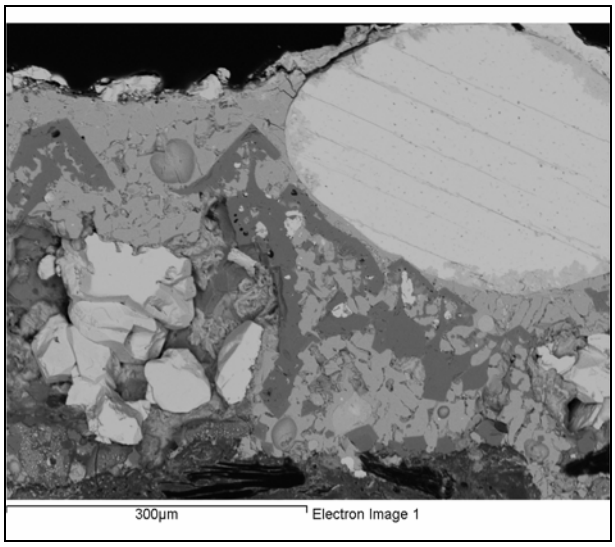


Fig. 5.13. *Crucible matte residue: large round prill of antimony; galena (white); tetrahedrite (light grey), magnetite (dark grey) (OB 519B/S1, BSE, 200x).*

Table 5.2 presents the chemical composition of crucible residues that are deemed to have originally constituted matte or metal rather than slag. Although these remains now clearly appear almost totally oxidised, this oxidation did not take place during the melt but is mainly post-depositional (Fig. 5.14). Their main phases are mostly composed of lead oxide, antimony oxide or both, with up to a few percents of silica, alumina, copper and iron oxides and lower amounts of alkali oxides and calcite. The higher levels of silica, alumina, alkali oxides, calcite and iron oxide in the bulk are generally concentrated in a variety of feldspathoid crystals (leucite $KAlSi_2O_6$, and silicates similar to lazurite $Na_3Ca(Al_3Si_3O_{12})S$) (Fig. 5.15), which grow in relatively silica-poor environments. The variable bulk concentrations of iron and sulphur are of relevance when trying to infer the original state of these samples before oxidation, i.e. whether they were matte or metallic bullion.

	Na_2O wt%	MgO wt%	Al_2O_3 wt%	SiO_2 wt%	SO_3 wt%	K_2O wt%	CaO wt%	TiO_2 wt%	FeO wt%	CuO wt%	ZnO wt%	As_2O_3 wt%	Ag_2O wt%	Sb_2O_3 wt%	PbO wt%
OB 307/S1	4.3	b.d.l.	13.6	17.5	2.9	1.8	2.7	b.d.l.	2.5	11.8	b.d.l.	b.d.l.	b.d.l.	b.d.l.	42.9
OB 307/S2	b.d.l.	b.d.l.	2.1	5.8	15.7	b.d.l.	1.4	b.d.l.	13.1	6.6	1.0	b.d.l.	3.1	8.7	42.5
OB 464/S1	4.0	0.8	5.8	11.5	b.d.l.	1.6	4.3	b.d.l.	7.6	b.d.l.	b.d.l.	1.2	b.d.l.	b.d.l.	63.2

Table 5.2. *Average chemical composition by SEM-EDS, normalised to 100 wt%, of the bulk of the oxidised crucible matte and bullion residues (b.d.l.: below detection limit).*

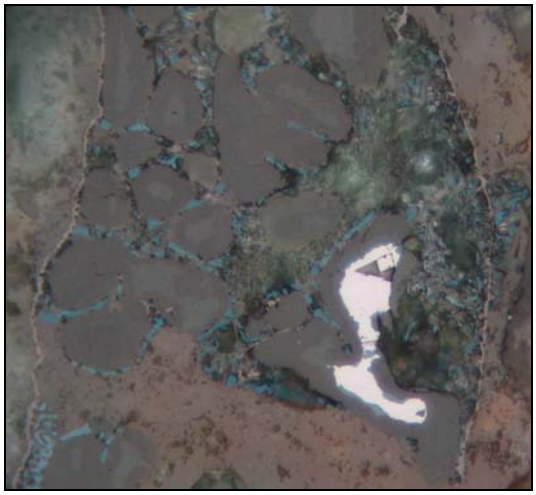


Fig. 5.14. *Corroded dendritic structure of what were originally lead and copper sulphides (OB 307/S2, optical microscope, plane polarised light, 500x, long axis ~250 µm).*

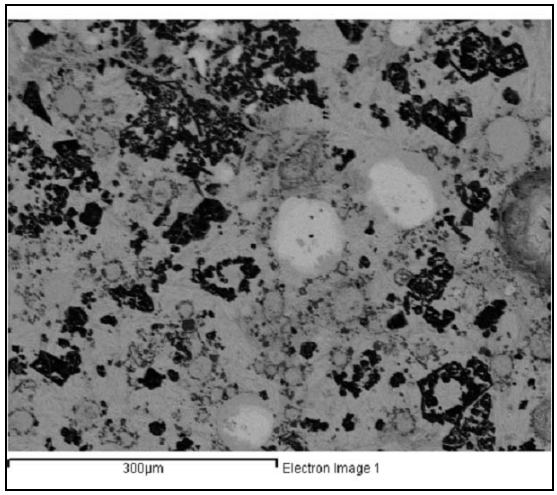


Fig. 5.15. *Numerous dark grey crystals similar to lazurite in a bright lead oxide-rich matrix. Note the less corroded copper- or silver-rich lead prills (white) (OB 464/S1, BSE, 200x).*

The bulk composition of specimen OB 307/S2 shows a high concentration of sulphur (16 wt% SO_3), suggesting that this crucible residue is most likely an oxidised matte (Table 5.2). This is confirmed by the metallographic study of this particular residue, which shows locally corroded dendritic structures and eutectic mixtures of sulphur-rich phases (Fig. 5.16). These structures are now chemically composed of lead sulphate dendrites and interdendritic copper sulphide (CuS). The dendrites were most likely originally lead sulphide, which was transformed after deposition of the artefact into lead sulphate. This is confirmed by the bright residual core of lead sulphide easily noticeable under plane polarised light, which is surrounded by the grey phase, indicating that it is progressively changing by corrosion into this phase of lead sulphate (Fig. 5.14). The primary copper sulphide might also have become a sulphate ($CuSO_4$) after the vessel was discarded, and subsequently leached out, due to its high solubility in water. Some secondary copper sulphide could have precipitated and deposited in the voids left if the environment was not too rich in oxygen. This corroded dendritic sulphidic structure is similar to that of the matte phases adhering to the top surface of lead bullion OB S003/S1, discussed below (Fig. 5.16).

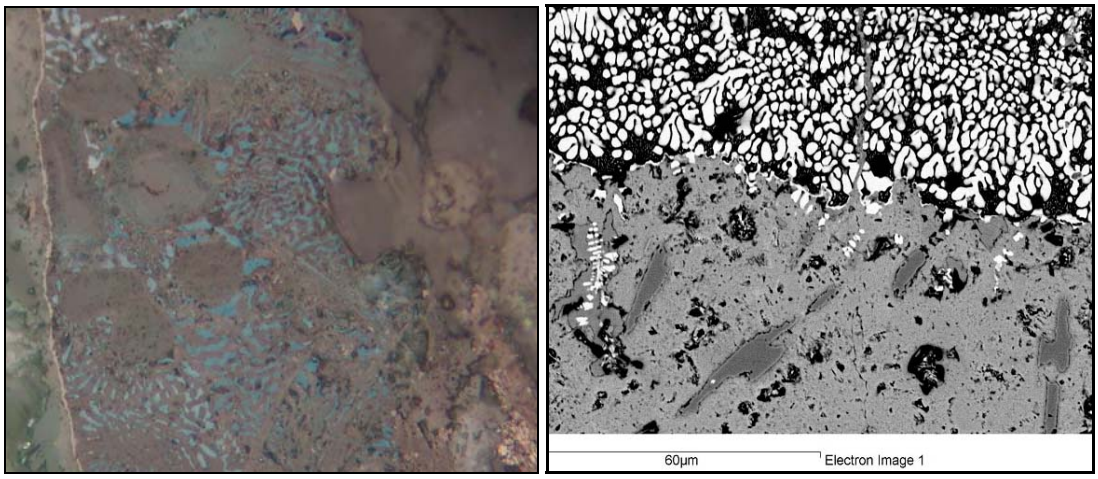


Fig. 5.16. *Left: eutectic mixture of lead and copper sulphide originally, now fully corroded (OB 307/S2, optical microscope, plane polarised light, 500x, long axis ~250 µm); Right: similar dendrites of lead sulphide and interdendritic copper sulphide above the metal phase of a lead bullion (OB S003/S1, BSE, 1000x).*

The residues OB 307/S1, removed from the lower part of the same crucible as previous specimen OB 307/S2, are mainly composed of lead oxide (43 wt% PbO), with significant levels of silica (18 wt% SiO_2), alumina (14 wt% Al_2O_3), copper oxide (12 wt% CuO), and lower amounts of soda (4 wt% Na_2O), calcium oxide (3 wt% CaO), iron oxide (3 wt% FeO), sulphur (3 wt% SO_3), and potash (2 wt% K_2O) (Table 5.2). The low iron oxide and sulphur bulk contents seem to indicate that these metallurgical remains are oxidised bullions layers. The microstructure of these remains comprises various phases of copper oxide; lead oxide (87 wt% PbO) – the balance being alumina (6 wt% Al_2O_3), copper oxide (4 wt% CuO), silica (2 wt% SiO_2), and magnesia (1 wt% MgO) – and silicates, which contain all of the alkalis and sulphur (Fig. 5.17). While this is most probably a fragment of bullion, there are yet many elements in the composition coming from the contamination by the slag, which would have partially been in contact with it. This remain however shows that the metals would be collected in a lead-rich metallic phase at the bottom of the vessel.

OB 464/S1 shows a significant concentration of lead oxide (63 wt% PbO in the bulk, 87 wt% PbO in the main phase) (Table 5.2); no sulphur has been detected in the bulk. An abundant number of lead metal prills are also detected; these are only slightly oxidised, because the lead is associated with copper (1 wt% Cu) or silver (3 wt% Ag), which seems to make it more corrosion resistant than the main matrix

(Fig. 5.15), and confirms that this sample was originally in a metallic state. This sample also shows one area of pure lead with a separate phase of pure copper metal.

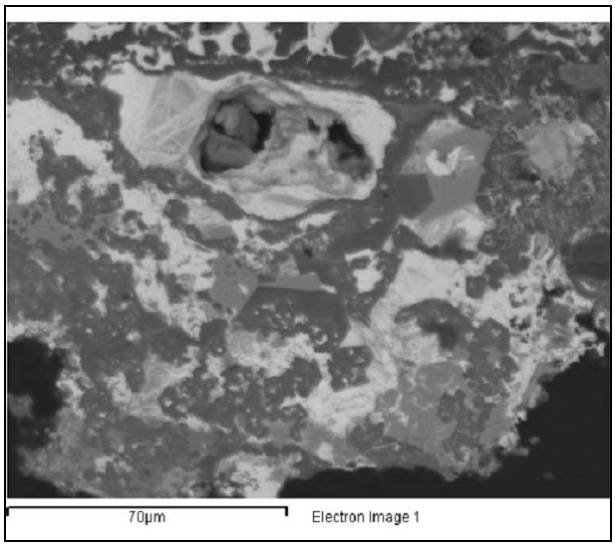


Fig. 5.17. *Microstructure of oxidised bullion remains: phases dominated by lead oxide (bright), copper oxide (medium grey), and silicates (dark grey) (OB 307/S1, BSE, 800x).*

5.2.1.3. Outer surface of crucible walls

Several crucibles display a thin slag layer on the outer surface, which is visually similar to the inner slag. This is there most likely due to some spillage, indicating that the melted charge was poured into another receptacle at the end of the operation, while still hot (Fig. 5.18). In other cases, the formation of this thin outer layer (0.2-0.3 mm) is simply due to the reaction of vitrified or bloated ceramic with contamination characteristic of the fuel ash, as seen in the elevated levels of alkali and alkali earth oxides (Table 5.3). The overall uniform vitrification and good state of most of the used crucibles implies that they were not in direct contact with the fuel, sitting among charcoals, as was the case in earlier times (Bayley 1996; Bayley 1997). It is more likely that they were either heated indirectly in a reaction chamber which was separated from the fire box, or that muffles were used. This is consistent with historical sources as well as with the archaeological evidence, e.g. the vitrification pattern on the bricks of the furnace remains (see below).

	Na_2O wt%	MgO wt%	Al_2O_3 wt%	SiO_2 wt%	P_2O_5 wt%	SO_2 wt%	K_2O wt%	CaO wt%	TiO_2 wt%	FeO wt%
OB 307/S1	3.8	6.6	10.7	57.1	0.7	0.6	5.4	7.6	0.6	6.9
OB N003/S1	4.8	4.4	10.3	52.0	1.0	b.d.l.	2.7	17.9	1.1	5.8
Average of ceramic matrices*	0.2	0.7	32.2	57.0	0.2	b.d.l.	2.1	0.6	1.4	5.6

***** after Martinón-Torres and Rehren 2005b

Table 5.3. *Average chemical composition by SEM-EDS, normalised to 100 wt%, of outer crucible slag samples (b.d.l.: below detection limit).*

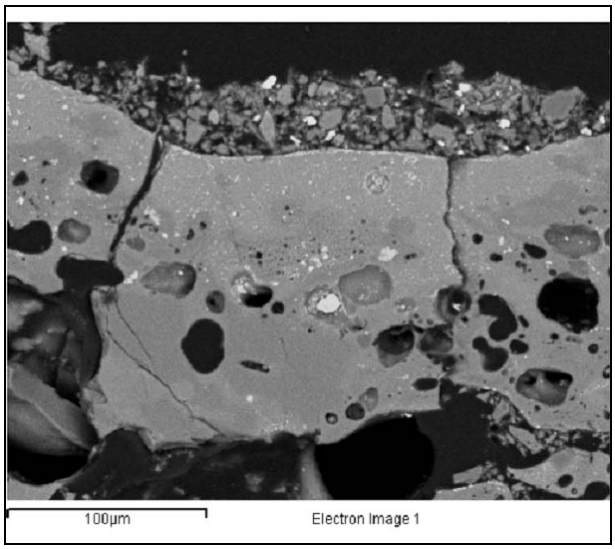


Fig. 5.18. *Outer slag of a crucible: lighter grey colour, numerous bright inclusions and a line of pores between the vitrified ceramic and this layer. Post-depositional surface layer on top of slag (OB 307/S1, BSE, 400x).*

Several muffles have been recovered from Oberstockstall (Von Osten 1998) (Fig. 5.1 p.111, 5.20). These are once again perfect matches to their corresponding sixteenth-century description, especially Biringuccio's (Fig. 5.19, left, at assayer's feet). As mentioned in the previous chapter, the use of muffles would help protect the charge in the vessels and the vessels themselves against contamination and corrosion by charcoal dust and ash. However, some fuel ash would be carried with the hot air underneath the muffle and thus reach the crucibles. The reaction of this dust with the ceramic of the crucibles then led to the formation of this thin coating layer enriched in lime, potash, and magnesia, which are typical of wood ash (Sanderson and Hunter 1981; Misra *et al.* 1993; Wedepohl 1997; Wedepohl 1998; Stern and Gerber 2004; Tite *et al.* 2006). Wood and charcoal, easily available in quantity, were acknowledged by Renaissance assayers as the best furnace fuel (Smith and Gnudi 1990: 173), and charcoal remains are abundant in the Oberstockstall assemblage (Von Osten 1998: 303).

As explained in chapter 4, a furnace configured with an empty lower space (ash pit), separated by a grid from the hot chamber which holds both the fuel and the reaction vessels, uses heating by convection, and therefore enables a better regulation of the temperature by means of hole plugs (Fig. 5.21, left), which can be inserted or removed to decrease or increase the air flow and therefore the temperature in the furnace. Many of these plugs have been found in Oberstockstall (Fig. 5.21, right), and the furnace brick remains had a more intense vitrification on the top surface, suggesting they were arranged in a structure of this type. Representations of such furnaces are given in various Renaissance technical treatises (Fig. 5.22).

Finally, some crucibles show a local contamination in iron oxide on the outer surface. One particular specimen (OB 307/S1) has a relatively large inclusion of an iron silicate (83 wt% FeO), situated at the top of the crucible. This confined surface enrichment in iron is probably due to contamination from the handling of the hot crucibles with iron tongues when taking them out of the furnace during and/or after the reaction, or during their spatial reorganisation in the furnace chamber with a rod (Fig. 5.19).

Fig. 5.19. *Left: An assayer using an iron rod to move the hot charcoal and crucibles in the assay furnace, by Biringuccio. Note the muffle at assayer's feet (after Smith and Gnudi 1990: 140); Right: iron tools leaning against a muffle furnace as depicted in Ercker's treatise (letter I) (after Sisco and Smith 1951: 76).*

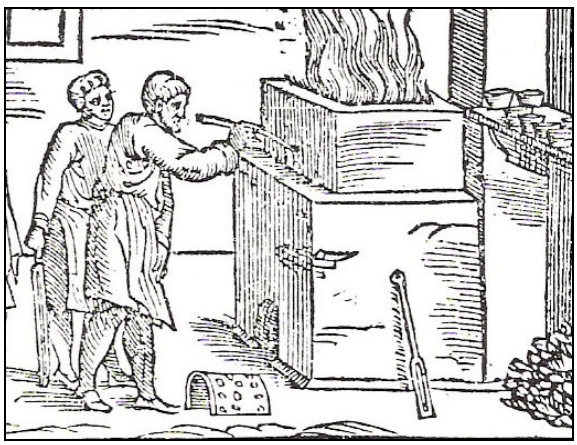


Fig. 5.20. *Examples of used (right) and unused (left) muffles from Oberstockstall, under which the reaction vessels would have been placed (scale bar 15 cm; photo: M. Martinón-Torres).*

Fig. 5.21. *Left: distillation furnace. Note the holes above letters A and E, and the plug on the floor (letter H) (after Sisco and Smith 1951: 145); right: example of ceramic plugs found in Oberstockstall. Note that the smaller one fits in the bigger, allowing a precise adjustment of the air flow (photo: M. Martinón-Torres).*

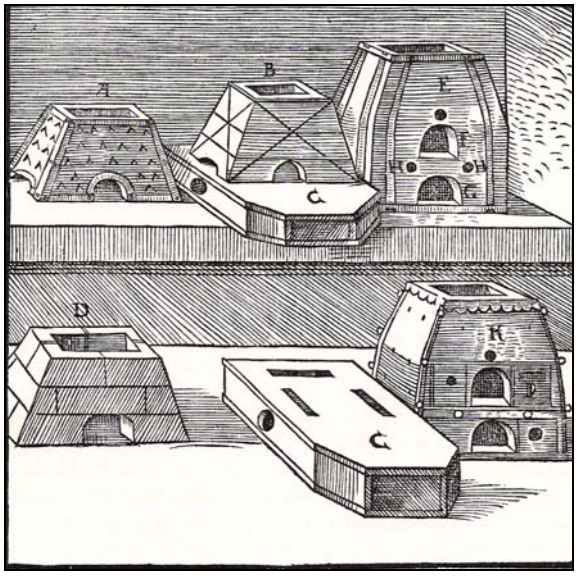


Fig. 5.22. *Assay furnaces as depicted by Ercker (after Sisco and Smith 1951: 23).*

5.2.2. Discussion: a relatively standard use of the crucibles

The samples described above contain a mixture of slag, matte and metallic remains found inside the triangular crucibles. From the analytical study, it becomes apparent that the materials processed in these crucibles were ores, and not some metals or alloys. Too many elements, such as iron, calcium, magnesium, titanium, zinc and antimony point towards a mineral origin, and cannot be explained as contamination from the ceramic fabric. Besides, some residual minerals are visible in several samples. Some of these particular components were most likely part of the ore itself, and others were probably added as fluxes or collectors. It will be argued that, in most cases, glass, salt and iron filings were added as fluxes, and lead as a noble metal collector. However, it will also be shown that besides what seems to be one main procedure, a variety of other operations were actually carried out in these crucibles.

5.2.2.1. The main pattern: the fusion of a sulphidic ore with crushed glass, salt and iron filings

The most informative crucible remains concerning the identification of the raw materials that were processed in these vessels are the matte residues and metallic phases included in the crucible slag. The results of their analyses will therefore be discussed first. These considerations will be followed by the interpretation of the

data regarding the bulk of the slag, which allows the determination of the potential ore gangue and/or fluxes added to the crucible charge.

- **Matte and metallic inclusions of the crucible slag residues**

The matte phases in the slag suggest the processing of a sulphidic ore, part of this sulphur not having been oxidised during the reducing fusion in the crucible, and forming phases separate from both the silica-rich and the metallic systems. The recurrence of antimony, copper, lead and silver implies the processing of a fahlore, a complex sulphidic ore ($(Cu, Fe, Pb, Ag)_{12}(Sb, As, Bi)_4S_{13}$), probably for its content in precious metals. The identification of zinc in various slag matrices, even in low concentrations (Table 5.1, p. 121), fits this idea, as sphalerite (ZnS) is a very common sulphide and frequently occurs with fahlores and silver ores. More generally, fahlores usually grow in association with base metal sulphides such as sphalerite, pyrite, galena, etc. The matte inclusions in the slag confirm that three layers probably formed in the crucibles: the lead-rich metallic bullion at the bottom, a sulphide-based system in between (the matte), and an oxide-based system on top (the slag). These three melts would separate by density in the crucible due to their non-miscibility in the liquid state. However depending on the overall viscosity of the melt, possible mixing during pouring, and the cooling rate, some sulphides and metal prills would be trapped in the slag, forming these discrete globules.

The main part of the lead detected in the matte and metallic residues most likely originates from the addition of metallic lead used as collector for the precious metals, although part of it may come from the ore itself, in the form of galena. The silver from the ore is mostly collected by the lead, while a small portion remains trapped in the matte. While the metal would be further processed to extract the silver, it appears that the slag was discarded; therefore any silver trapped in the matte cakes and in matte or metal globules within the slag would be lost. Thus, if the results of the assay were to be quantified, the amount of silver in the ore would be slightly underestimated. It will be shown later in this chapter, however, that matte was probably also occasionally scorified with some additional silver-free lead, so the amount of silver present in this phase would be quantified as well. Matte may have also been refined together with the lead bullion in a scorifier if the overall purpose of the operation was to quantify the noble metal content of the ore, without a specific focus on either of the two phases, matte or bullion.

The metallic prills give further information about the metals which were extracted from the ore(s), containing antimony, copper and silver. As stated above, despite the other metals, the occurrence of silver, in the broader context of other refining equipment such as cupels, strongly supports the idea of the assay of ores for their silver content.

- **Crucible slag remains**

There are several possible origins for the crucible slag, which are not mutually exclusive. Some of the crucible ceramic could have melted during use and contributed to the slag formation. However, not all the elements present can be explained by this scenario. The slag is relatively rich in iron when compared to the ceramic matrices of these crucibles (Martinón-Torres and Rehren 2005b): the SiO_2/FeO ratio is *ca.* 11 in the ceramic while it only varies from *ca.* 2 to 9, with an average of *ca.* 4, in the slag, meaning there is almost three times more iron than expected, if the slag were simply fused ceramic (Fig. 5.23). A similar situation is visible for the calcium oxide concentration, which is about eight times higher than it would be if originating from the ceramic only: the SiO_2/CaO ratio is *ca.* 82 in the ceramic while it ranges from *ca.* 2 to 13 in the slag, with an average of *ca.* 6 (Fig. 5.24). Furthermore, the SiO_2/Al_2O_3 ratio is higher in the slag (*ca.* 6) than in the ceramic (< 2) (Fig. 5.23). This could result from either a selective melting of the ceramic fabric and/or, more likely, an additional source for silica, especially for the crucibles showing a clean-cut interface between ceramic and slag and therefore no significant chemical interaction between the two. Thus, the contribution from the ceramic to the slag is very limited. Finally, we know that unused crucibles are free of zinc, antimony and lead (Martinón-Torres and Rehren 2005b), so these are clearly elements that formed part of the charge and, in turn, contaminated the crucible fabric.

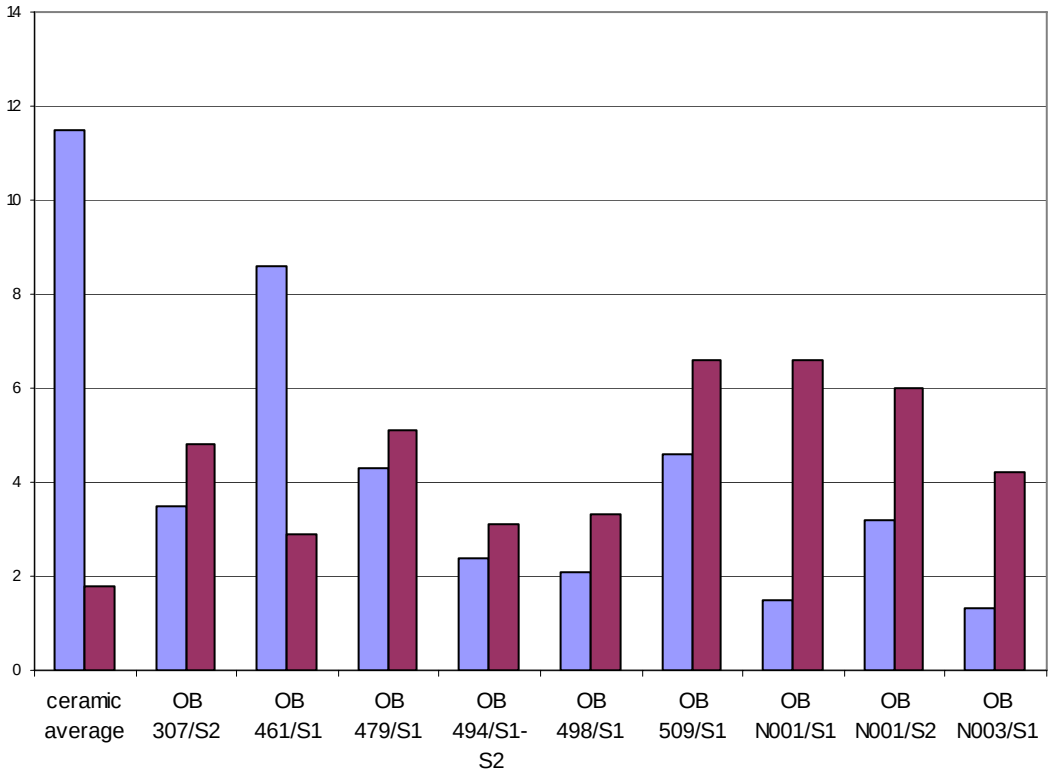


Fig. 5.23. *Diagram comparing the SiO_2/FeO (blue) and SiO_2/Al_2O_3 (purple) ratios between the ceramic fabric (wt% of oxides averaged after Martinón-Torres and Rehren 2005b) and the glass matrix of the crucible slag specimens.*

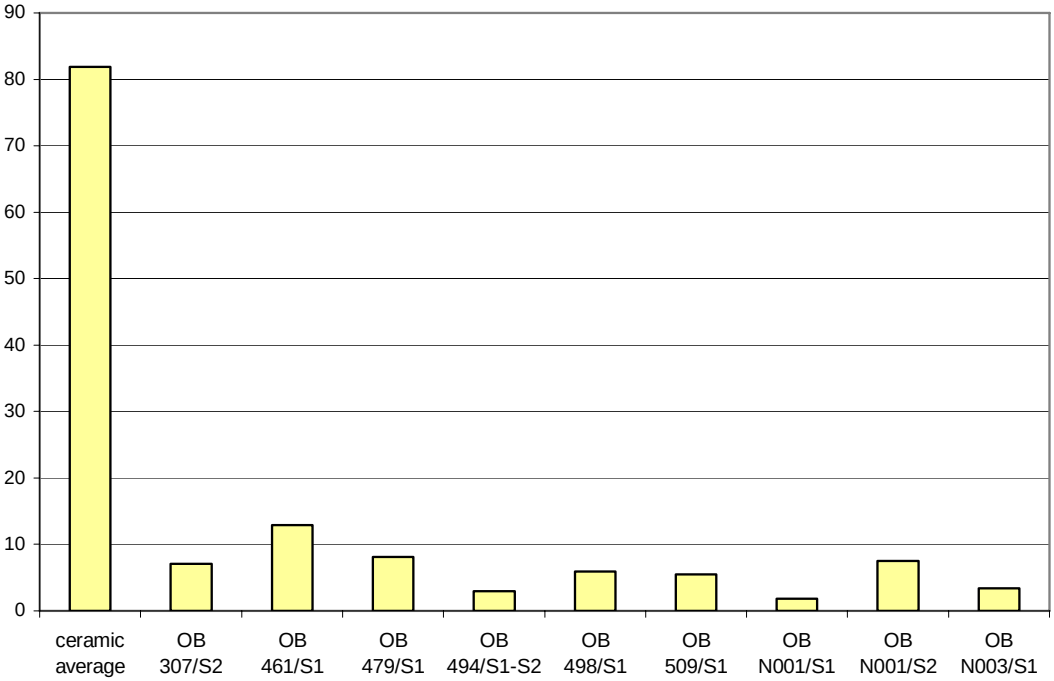


Fig. 5.24. *Diagram comparing the SiO_2/CaO ratio between the ceramic fabric (wt% of oxides averaged after Martinón-Torres and Rehren 2005b) and the glass matrix of the crucible slag specimens.*

On this basis, it can be argued that the gangue of the ore tested could have been rich in quartz and/or calcite, enriching the slag in silica and calcium oxide. Quartz is a common gangue mineral for many ores – in particular gold ores and several sulphidic ores –; and both quartz and calcite are the gangue of many copper ores and complex sulphidic ores such as fahlores. Biringuccio mentions limestone as a gangue mineral of copper ores and silver- or gold-bearing lead ores (Smith and Gnudi 1990: 53). Furthermore, although Agricola explains that adding lime – among other reagents – could be of help in smelting poor ores (Hoover and Hoover 1950: 388-390), evidence seems to show that, in the present case, glass was more plausibly added instead of limestone or calcite (see below). The high levels of calcium oxide in the slag may thus be the result of an accidental or intentional introduction of gangue fragments attached to the sulphidic minerals to the charge and/or the addition of glass, in which calcium oxide is used as stabiliser, as flux.

Besides the partial fusion of the crucible fabric and the presence of siliceous gangue, other potential sources for the silica in the slag may be considered. Another source could be a silica-rich flux added to lower the melting temperature of an iron-containing ore, by forming more easily melted iron silicates. Agricola recommends adding "stones which melt easily in the fire", among which he counts quartz, to smelt ores that "heat and fuse slowly" (Hoover and Hoover 1950: 380). This would be the case for a refractory zinc- and iron-containing ore with a calcite gangue, such as the one tentatively identified in these crucibles. Lastly, following some of the contemporary writers (Hoover and Hoover 1950: 238; Smith and Gnudi 1990: 143, 333), the chymist working in Oberstockstall may have used crushed glass as a flux or part of a mixture of fluxes. This could explain the combined high concentrations of silica, potash and lime in the slag (Table 5.1, p. 121). Although these element concentrations show no positive correlation, this is probably due to the tendency of potash to evaporate at high temperature, and to the fact that, as mentioned above, gangue minerals could also have contributed to the lime and silica levels in the slag. It should also be noted that the amount of potash in some of the slag cannot be explained as a result of ash contamination alone, since it has previously been shown that the crucibles were heated from the outside and the quantity of charcoal ash that would be required to produce such enrichment is not conceivable in crucibles of this size range. Lime could partly come from the gangue as well as from the glass. Early modern glass typically contains more lime than alkali oxides (Wedepohl 1997;

Wedepohl 1998), and was readily available at the laboratory of Oberstockstall. Thus, the raised silica levels could originate from the addition of glass to the charge. There may have been further additions of glass or quartz in the course of the reaction, but the complexity of the resulting slag system does not allow to clarify this.

Turning to the iron content in the slag, this probably originates from pyritic ores, the most common sulphides. Gold often occurs disseminated in veins of pyrite or arsenopyrite, and a crystal of arsenopyrite, a minor ore for gold, has been identified by Soukup and Mayer (1997) in the assemblage of Oberstockstall. It may be worth noting that, due to its apparent similarity with gold, pyrite is widely known as the 'fool's gold' or the 'gold of the alchemists'. This element also fits the structure of fahlores, potentially the main ore processed at this site. However, iron could also have been added as a flux to drive the ore to melt. As already mentioned, Ercker advises the addition of iron filings, that is metal, if the ore does not contain enough of it (Sisco and Smith 1951: 114). At estimated furnace temperatures (1100-1200 °C), metallic iron would react with silica, alumina and other gangue materials, to form a relatively fluid slag, which would allow an easier and finer separation of the different phases. When smelting gold-rich pyrites on a small-scale in a crucible, Agricola recommends iron filings or hammer scales to be used in addition to antimony sulphide, copper filings and lead as flux; he also uses iron scales as a flux combined with lead oxide-rich additives when smelting poor gold ores on a large scale in the blast furnace (Hoover and Hoover 1950: 397-398). The latter method described by Agricola is probably not what is documented in the Oberstockstall crucibles analysed here, given that if iron oxide from the slag was to react with a sulphidic ore at high temperature, the sulphur would drive off and the formation of sulphur-rich matte, as documented in the archaeological material, could not have taken place. Besides, these recipes are given in the context of smelting, though on both scales, but are not particularly duplicated in the chapter dedicated to assaying. Nonetheless, although this procedure is relatively unlikely to have been regularly performed, it may have been experimented with. Starting with such oxide-rich additives would make the formation of a thick matte layer possible only if the sulphur included in the ore was contained within the crucible, e.g. by a quickly formed slag layer or the addition of glass or salt, which would act as a cover for the melt and retain most of the sulphur. This phenomenon has been observed by Rostoker *et al.* (1989) in their experimental co-smelting of oxides and sulphides,

during which copper minerals were reduced to metal, and matte formed when some slag was added as a flux on top of the charge. However, it remains very difficult to further establish which chemical reactions would control the system, since these would depend on their mechanisms and kinetics at the estimated temperatures. Overall, all one can say from the slag analyses is that iron could be part of the ore, the flux or both.

The bulk soda content in the glass matrices of the crucible slag varies between 3 and 7 wt%, which is much higher than the concentration in the ceramic matrix. This, together with the fact that the few feldspar inclusions of the crucible fabric are mostly potassium-based, clearly demonstrates that this soda enrichment in the slag does not find its origin in the ceramic. Besides, the Na_2O/Al_2O_3 molar ratio in the slag glass ranges from 0.2 to 4.0, with an average of *ca.* 1.3 (Table 5.1, p. 121). This ratio being generally higher than 1 seems to indicate that sodium has not been introduced by accident, e.g. from a feldspar ($NaAlSi_3O_8$, Na_2O/Al_2O_3 molar ratio = 1), but intentionally added (I. Freestone, pers. comm.). This sodium-rich raw material could have been common salt, some sodium carbonate or nitrate, as recommended by the main Renaissance authors. These salts would act either as a cover for the charge, which would help prevent projections and therefore losses at the beginning of the reaction, or as a flux, because they would immediately melt in the hot crucible and drive the rest of the charge to melt. The hypothesis of the addition of rock salt as a flux seems to be supported by the apparent correlation between sodium and chlorine levels in the contaminated fabric of several used crucibles (Martinón-Torres 2005: 111) The concentration of chlorine in the various glass matrices of the slag, which is mostly around 1 wt%, could also be an indication of this use of rock salt. The amount of chlorine ions soluble in a glass is however limited by the structure of the glass itself to *ca.* 1 wt%, additional chlorides then forming a separate melt (Tanimoto and Rehren 2008). The glass matrix of the slag thus appears saturated in chlorides, which suggests that chlorine was not introduced in the glass from the burial environment but results from an intentional addition of a chlorine compound, which would have most likely decomposed at high temperature and individual ions would have then entered the glass matrix of the forming slag. This observation may, however, still not be a good enough confirmation of the addition of rock salt, since there may be another or additional source for sodium in the form of soda-lime-silica glass. It needs to be remembered here that, although

potash-lime-silica glass was the main glass type used during the Renaissance in northern Europe, soda-lime-silica glass was regularly imported from Italy, particularly Venice (Henderson 2000: 90-100). The high amount of sodium oxide in the slag could therefore also be due to the addition of such type of glass. This would be in conformity with the occurrence of Venetian glass objects in the assemblage from Oberstockstall (Von Osten 1998: 70). As mentioned above, the use of glass as flux seems to be suggested further by the high levels of calcium oxide in the slag.

In summary, based on the analytical results, it appears that a relatively large number, and possibly the majority, of the triangular crucibles in the laboratory assemblage from Oberstockstall was used for the reducing fusion of sulphidic minerals, such as tetrahedrite, pyrite or galena, having a gangue composed of calcite and/or quartz. Most likely, several fluxes were added to the charge and contributed to the simultaneous formation of metal, matte and slag. Lead was probably introduced as collector for the noble metals, but it may have also been part of the ore, since galena is a common mineral occurring in sulphidic argentiferous ores. Similarly, iron may have been used as a flux: adding iron metal to a fahlore, such as tetrahedrite, would produce pyrrhotite as well as metallic copper and antimony, since iron would preferentially combine with sulphur and facilitate the reduction of the base metals in the ore. Iron can also originate from a second source, as it could have been a potential component of the ore to be tested. Potash and soda present in the slag are probably not elements from the ore, and were almost certainly part of additional reagents. Fluxes such as glass, iron filings and some salts were probably added to the ore to perform the first stage of the metallurgical sequence under reducing conditions.

Altogether, this reconstruction is consistent with written sources; Biringuccio, Agricola and Ercker all recommend the use of various fluxes for the reducing fusion and testing of ores (cf. chapter 4). Of these, some glass and salt – probably a combination of potash-rich glass with rock salt or sodium carbonate, or some soda-lime-silica glass with saltpetre or potassium carbonate or a mixture of all these –, together with iron filings seem the most likely possibilities here, helping the melting of a fahlore.

Although contemporary texts aid the interpretation of the archaeological remains, there are, however, some major differences between contemporary metallurgical

texts and laboratory practice as documented in Oberstockstall. One of the most remarkable differences appears to be the roasting stage, recommended by the former when processing sulphidic ores, and apparently absent in the latter, which led to the formation of crucible matte. These similarities and differences will be discussed in more detail later (cf. chapter 7).

- **Oxidised crucible bullion and matte phases**

Oxidised bullion and matte remains were identified within the triangular crucibles, as presented in the analysis above. The differentiation between oxidised matte and bullion residues was possible based on the thorough characterisation of the matte cakes and fragments (Fig. 5.7, p.116), which is described in more detail below. As will be seen, these isolated pieces of matte usually show a similar microstructure to each other, i.e. a complex mixture of sulphur-based phases, mainly composed of iron, copper, antimony, and lead, with many magnetite crystals and entrapped metallic prills of antimony and/or copper, and slag particles.

The low bulk sulphur content (3 wt% SO_3) of specimen OB 307/S1 seems to indicate that the metallurgical remains of this crucible are from an oxidised bullion. This is reinforced by the oxidised phases of lead and copper, which do not show any residual sulphidic core, contrary to the clear matte phases of OB 307/S2, which are now present as sulphates. Thus, the existence of both metallic and matte residues in the same vessel– as well as a slag layer (Table 5.1, p. 121) – verifies the hypothesis of the formation of three layers in the triangular crucibles.

Based on its lead-rich matrix (87 wt% PbO), the residue removed from the inside of crucible OB 464 seems to be a lead bullion, now partly oxidised. The separate phases of pure oxidised lead and pure copper confirm the metallic origin of this layer and the most likely use of lead as metal collector. It is clear that this formed under a matte layer, due to its numerous inclusions containing sulphur in high concentration. Contrary to most of the metallic and sulphidic remains, this sample has no antimony, but a high arsenic level instead (4 wt% As_2O_3 in the matrix). This again supports the idea of an ore as the raw material to have been processed in these crucibles, since fahlores are either dominated by antimony (tetrahedrite) or arsenic (tennantite). According to this, the sample tested here was probably of the tennantite family, therefore slightly different from the bulk of the raw materials identified in this laboratory, which are usually richer in antimony. Nonetheless, the high local

concentrations of silver (4 wt% Ag) in the lead prills indicate that this ore was also processed for its content in noble silver, similarly to the antimony-rich ores. In addition, this particular sample shows that in a bullion produced from an ore devoid of antimony and dominated by another element, such as arsenic, antimony is not detected at all, which further indicates that in the samples where antimony has been detected, it most likely originates from the ore. This seems to rule out the possibility of antimony sulphide being routinely used as a flux or an additive, such as precious metals collector, as advised by Agricola and Ercker (cf. chapter 4 and see above). If stibnite has, however, been used for the processing of antimony-dominated fahlores, it would not be possible to infer from the present data.

From this discussion of the results obtained on eight crucibles out of eleven studied, a main utilisation of the triangular crucibles seems to emerge, as a first step in a longer sequence leading to the processing of fahlore-rich ores through dry high-temperature reactions to test their content in noble metals. However, three other samples have illustrated a wider range of procedures and techniques also performed in Oberstockstall. Some examples of these various metallurgical activities are presented below.

5.2.2.2. Some peculiarities: a glimpse of variability in the operations

- **The processing of a different ore**

The slag residues from crucible OB 345 display a different microstructure: they have a glassy slag notably enriched in titanium oxide and calcium oxide (Table 5.4), and inclusions of residual quartz, titanite ($CaTiSiO_5$) and fluorine apatite ($Ca_5(PO_4)_3F$) (Fig. 5.25). This specific slag composition suggests the processing of a mineral different from the one identified above for most of the slag remains. This source could have been an ore whose gangue was made of titanite, apatite, and quartz, rather than quartz and calcite as suggested from the results of the main set of samples. The various residual minerals of this slag, only partly dissolved in the glass, are unlikely to come from the erosion of the ceramic. Titanite is non-existent in the ceramic fabric and apatite is too rarely found to contribute on its own to the large number of crystals of this mineral in the slag. Doubts only remain on the quartz inclusions, since quartz grains constitute the most abundant inclusion in the ceramic

fabrics, making up to a quarter of the total volume (Martinón-Torres 2005: 111; Martinón-Torres and Rehren 2005b).

	Na_2O wt%	MgO wt%	Al_2O_3 wt%	SiO_2 wt%	P_2O_5 wt%	K_2O wt%	CaO wt%	TiO_2 wt%	FeO wt%	CuO wt%	ZnO wt%	Sb_2O_3 wt%	PbO wt%	SO_2 wt%
Glass matrix of slag layer	3.9	2.0	13.4	55.2	0.9	3.3	8.4	5.7	6.5	b.d.l.	0.1	b.d.l.	b.d.l.	0.6
Bulk of matte residue	b.d.l.	1.1	1.6	12.4	b.d.l.	b.d.l.	5.2	1.6	24.4	b.d.l.	b.d.l.	24.0	21.8	7.9
Main phase of matte residue	0.3	0.5	0.8	6.7	b.d.l.	b.d.l.	3.8	0.8	6.4	0.7	b.d.l.	38.4	41.6	b.d.l.

Table 5.4. *Average chemical composition by SEM-EDS, normalised to 100 wt%, of the slag layer and oxidised matte residues of crucible OB 345 (b.d.l.: below detection limit). See appendix 2 p.312 for the full results on the glassy matrix of the slag layer.*

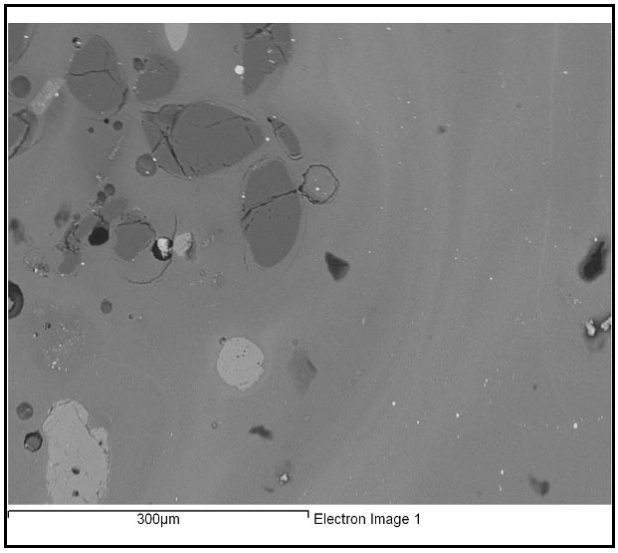


Fig. 5.25. *Slag composed of a grey glass and residual crystals of quartz (dark grey) and titanite (light grey). Note the various shades of grey around the remaining minerals, indicating they are gradually dissolved in the glass matrix (OB 345/S1, BSE, 200x).*

Many crystals of magnetite can also been identified, close to the top surface of this slag. These display bright lamellae of haematite, indicating that close to the rim, where this sample is from, the conditions were oxidising. The charge, however, was probably melted under reducing conditions, as implied by the dendrites of pyrrhotite, occurring in the corroded matte remains of this sample. The significant iron content of this oxidised layer of matte (24 wt% FeO; Table 5.4) is visible in the presence of these numerous dendrites of pyrrhotite, some of which have oxidised in the fire to form the magnetite crystals previously mentioned (Fig. 5.26). The latter have developed in the liquefied charge thanks to the reaction of pyrite and its burnt counterpart pyrrhotite, which were probably partly composing the matte, with the

oxygen available from the forming slag. That is why the magnetite crystals can now generally be seen at the interface of this oxidised matte with the slag.

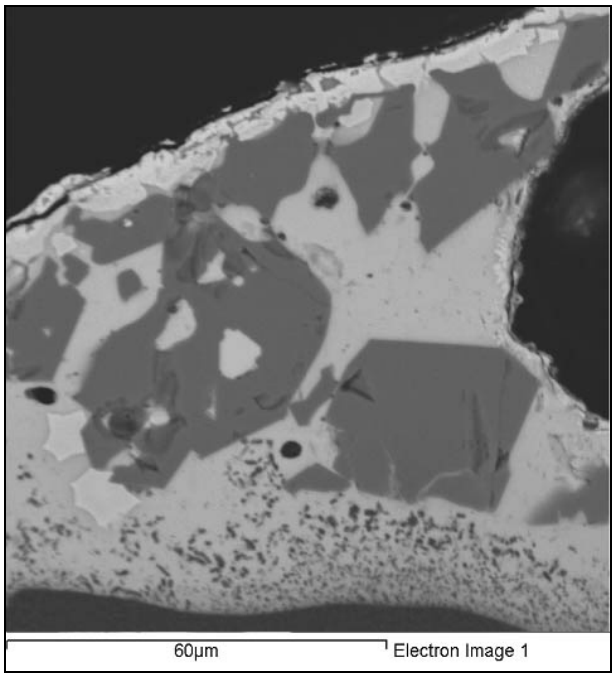


Fig. 5.26. *Large dark grey crystals of magnetite in a bright matrix rich in the oxides of lead and antimony (OB 345/S1, BSE, 1000x).*

- **The oxidising melting of a lead bullion**

The bulk of crucible residue OB 472/S1 is very rich in lead and antimony oxides (44 wt% PbO, 38 wt% Sb_2O_3), with relatively high levels of silica (9 wt% SiO_2) and alumina (5 wt% Al_2O_3), in addition to a little potash (2 wt% K_2O), calcium oxide (1 wt% CaO) and soda (1 wt% Na_2O) (Table 5.5). The bulk sulphur concentration of this sample is too low to be detected; sulphur is only identified in the numerous crystals of leucite and lazurite-like feldspathoids separate from the main matrix of lead and antimony oxides (50 wt% PbO, 43 wt% Sb_2O_3) (Fig. 5.27); furthermore no copper or iron were detected in this sample, contrary to the matte residues described above.

	Na_2O wt%	Al_2O_3 wt%	SiO_2 wt%	K_2O wt%	CaO wt%	Sb_2O_3 wt%	PbO wt%
Bulk	0.7	5.1	9.2	2.0	1.5	37.8	43.7
Main phase	b.d.l.	1.5	5.2	b.d.l.	b.d.l.	43.1	50.2

Table 5.5. *Average chemical composition by SEM-EDS, normalised to 100 wt%, of the bulk and main phase of crucible OB 472 (b.d.l.: below detection limit).*

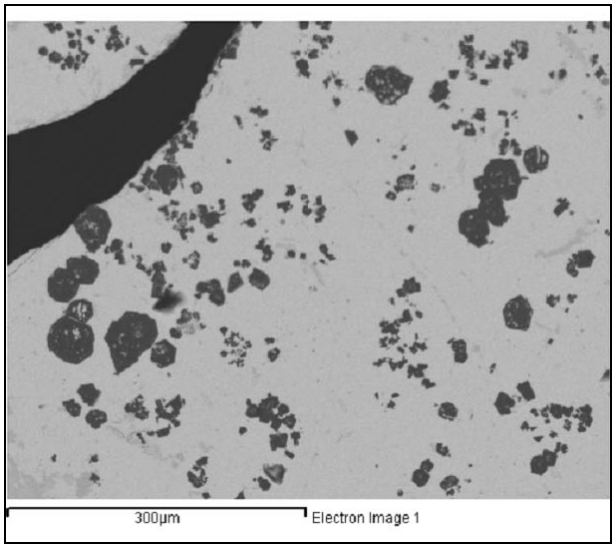


Fig. 5.27. *Numerous dark grey crystals similar to leucite and lazurite in a bright matrix rich in the oxides of lead and antimony (OB 472/S1, BSE, 200x).*

The overall richness in lead and antimony, the low sulphur content, and the absence of copper and iron suggest that the residue from crucible OB 472 is almost certainly an oxidised bullion. This is further verified by the analysis – presented below – of the matte cakes, which are relatively rich in iron, and the isolated lead bullion find, whose bulk is mainly composed of lead and antimony. The unusual number of feldspathoid crystals forming in a relatively silica-poor environment points towards the use of alkali-rich fluxes, since a metallic bullion on its own could not be the source for these specific elements in such a significant concentration. This again suggests that potassium, sodium, calcium and silica were intentionally added, with part of the silica and alumina probably coming from the ceramic. The high levels of these elements in these crucible slag remains strengthen the hypothesis that glass and salt were added to the charge, and are therefore probably responsible for most of this enrichment. The presence of the leucite and lazurite-like crystals in the oxidic matrix also indicates that the oxidation of lead and antimony is not post-depositional but took place under high temperature. The microstructure and elemental composition of this sample seem to indicate a different operation: this procedure could have been the oxidising melting of a bullion with glass and salt, this bullion having been produced in a triangular crucible beforehand through the main reaction, characterised above, of the reducing fusion of a sulphidic ore.

This procedure may have been the cleaning operation of a bullion to remove the residual matte, which may still be attached to it or contaminating it in the form of inclusions. Such a procedure would however produce an iron oxide-rich slag, which is not the case from the analytical data. If such an operation was carried out in this

laboratory, the present sample may reflect a final and possibly unnecessary refining of an already clean bullion, which would be devoid of matte and therefore not contribute iron oxide to the slag. There is however no real possibility to confirm the intention of the application of this process in light of the present data and one can only conjecture such a purpose.

- **The use of antimony as a collector for noble metals**

The crucible OB 479 has some remaining mixture of matte and metal, which is still attached to its slag. The bulk of the metallic residue is composed of copper (50 wt% Cu) and antimony (13 wt% Sb), now corroded to oxides (19 wt% O) and chlorides (15 wt% Cl). Copper forms the main matrix (56 wt% Cu, 25 wt% O, 19 wt% Cl), in which separate antimony-rich phases can be seen (57 wt% Sb, 19 wt% Cu, 14 wt% O, 10 wt% Cl) (Fig. 5.28). In this metallic environment, some corroded and round matte inclusions of copper sulphide can also be noticed (70 wt% Cu, 16 wt% S, 9 wt% Cl, 5 wt% O).

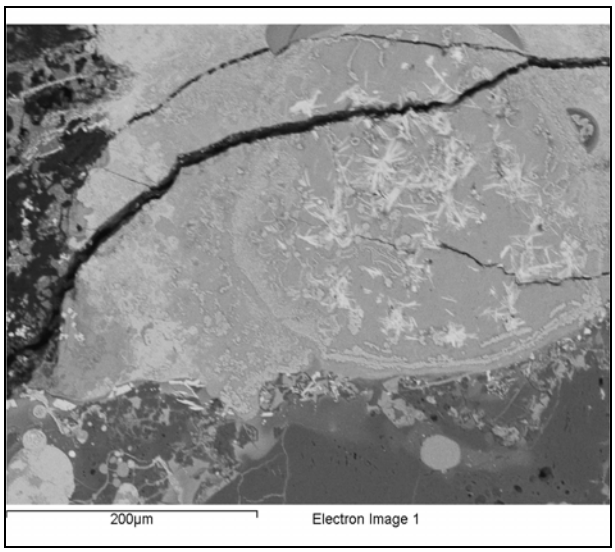


Fig. 5.28. *Metallic residue composed of a copper-rich matrix and bright antimony-rich phases (OB 479/S1, BSE, 250x).*

The slag layer in this crucible has a particularly high concentration of antimony oxide (41 wt% Sb_2O_3), whilst it is completely devoid of lead (Table 5.1, p. 121). This might be an indication of an even wider range of materials used at Oberstockstall, perhaps including antimony sulphide, which could have been used as a flux, if following one of Ercker's recipes (Sisco and Smith 1951: 114). This residue may also indicate an attempt to use antimony as a collecting agent for the noble metals, possibly considering it a 'type of lead' due to the similarity in

appearance and properties between both metals. It is important to emphasise that, in the sixteenth century, the nature and properties of antimony were not understood. Antimony is mentioned by Biringuccio (Smith and Gnudi 1990: 91-92) and Agricola (Hoover and Hoover 1950: 400, 428), but they do not recognise it as a metal and usually use the same word – *stibium* – for the metal itself and its sulphide. Ercker does not acknowledge it as a metal either: "[a]lthough there are other additional mineral ores that can be liquefied and smelted, such as bismuth, sulphur, antimony, and so forth, the aforesaid seven [metals: gold, silver, mercury, copper, iron, tin, and lead] head all the other *minerals* as the most important ones." (Sisco and Smith 1951: 4, my italics). This specific matter of awareness and understanding of the various materials and operations by the individuals using the laboratory of Oberstockstall will be discussed more broadly in a later section (cf. chapter 7).

In the sixteenth century, stibnite was in metallurgy mainly used for the parting of noble metals (Hoover and Hoover 1950: 451-452; Smith and Gnudi 1990: 201-202). The principle of this method is based on the greater affinity of silver for sulphur than antimony. Antimony plays the role of sulphur donor and gold collector, while silver preferentially reacts with sulphur. Two separate phases of silver sulphide and a gold-antimony alloy form in the hot crucible, with the metallic phase settling at the bottom. The corroded metallic residue of crucible OB 479, however, does not appear to illustrate this operation, since it contains too much copper in it, which would otherwise have been removed from the gold-silver bead through cupellation.

This crucible also presents another particularity: a relatively homogeneous layer in between the ceramic and the slag itself, which is highly enriched in potash (13 wt% K_2O) compared to its two surrounding phases (3 wt% K_2O in ceramic bulk, 7 wt% K_2O in glass matrix of slag). This layer could have been deliberately added by the potter to the ceramic: a feldspar lining may have been applied to the crucible wall possibly in order to protect the vessel itself against corrosion or attack by the reagents used in metallurgical operations, similarly to glaze layers in stoneware (Gaimster 1997). This would seem however rather strange, knowing that all the graphitic crucibles bear the same stamp and therefore come from the same ceramic workshop. It would appear unusual to have one unique crucible having this specific layer, while the others do not and still perform their function well, withstanding the heat and the attacks from chemical reagents. Besides, the feldspar lining would probably be easily melted by the crucible charge rather than protect the crucible,

suggesting further that the presence of such a lining is rather unlikely. Another explanation would be the addition in this case of a great quantity of saltpetre (potassium nitrate), instead of a sodium-rich salt, used as a cover for the charge. This potassium nitrate may have reacted with the hot ceramic wall, forming this glazing on the surface of the crucible wall.

5.2.3. Summary on the triangular crucibles

In summary, the typical operation carried out within triangular crucibles in this laboratory appears to be the reducing fusion of a complex sulphidic ore, which contained antimony, copper, iron, lead, and some silver, as well as some calcareous or quartz-rich gangue. From the scientific study of the various crucible remains, it appears that lead would have been used as a collector, and iron filings (metallic iron), salt and some crushed glass were possibly added to the charge as fluxes to melt this ore. Such a melt would produce a lead-rich bullion containing most of the metals, a sulphur-rich matte, and a slag mainly enriched in silica, iron oxide, calcium oxide, potash and soda, as it has been identified here.

Some possible variations to this main procedure have been identified. First, there seem to be alternatives for the ore: one being potentially rich in arsenic rather than in antimony, and another having a different gangue, composed of titanite, apatite, and possibly quartz.

The triangular crucibles may have been used to further process lead- and antimony-rich bullions under oxidising conditions, probably in order to reduce their weight and produce more slag so as to remove more impurities such as non-metallic elements from the bullion. This could have been done in a triangular crucible, as documented here and in which the fluxes would have worked more efficiently. However, if this was the actual aim, it does not seem to have been achieved properly in the case documented here, since the oxidised bullion remains still contain many of these slag phases.

Finally, the identification of a different metallic bullion residue, principally composed of antimony, which suggests the use of antimony as metal collector, emphasises the experimental nature of these various metallurgical and chemical reactions. It also raises the questions regarding the level of awareness of the individuals working in this laboratory, and to what extent they knew about the

procedures and materials they were dealing with in the way we do today. The peculiar potash-rich layer lining the inner surface of this particular crucible suggests that antimony was recognised as a distinct material and, as such, treated in a different way. Although the close similarities between lead and antimony may have precluded a full understanding of both metals in a modern way, this instance may illustrate some of the early experiments that would lead to the discovery of new elements and, in the long run, a renewed understanding of nature.

As argued later, the lead bullion produced in the triangular crucibles through the fusion of an ore would then be scorified, probably several times, before being cupelled. The slag would be discarded, while the matte may have been kept in the laboratory for further refining. Before moving to the subsequent stages, however, a detailed characterisation of the discrete lumps of matte and slag will be presented, as they reinforce the foregoing interpretation of the crucible uses.

5.3. Matte and bullion finds

Several matte cakes and fragments have been recovered in Oberstockstall. They are in relatively small quantity compared to the hundreds of reaction vessels. However, they are almost the only surviving proper products resulting from the high-temperature operations carried out in these ceramics, except for one fragment of slag and a single piece of bullion; all other remains are present only as relatively thin films attached to crucibles. A few metallic pieces, such as a hemispherical and heavy lead 'ingot' or lump, a tin-rich fragment and a triangular piece of metallic copper were also discovered as part of this archaeological record; it has not been possible to achieve any satisfactory interpretation regarding these metal lumps so far. Sheets of metallic lead were also found; these were probably the lead used as a noble metal collector. The occurrence of these various materials in the archaeological assemblage of this site suggests that they may have been kept for further treatment, while the scarcity of the slag suggests that it could have been thrown elsewhere [2].

The matte finds are thus the best-preserved physical representation of actual sixteenth-century laboratory practice, and their study is crucial to understand the chemical reactions, and help further in identifying the ore and the potential fluxes

[2] A later discussion will explain how this excavated pit was almost certainly not the everyday waste pit of the laboratory itself, but a ditch where the operating content of the laboratory was disposed of when the metallurgical activities there stopped (cf. chapter 7).

utilised by the individuals working in the laboratory of Oberstockstall. The microstructure and chemical composition of one piece of lead bullion and six matte finds were thoroughly investigated to address this, and the detailed results of their analyses are presented and discussed below. These results will be compared to the residues found attached to the crucibles in order to test their mutual correspondence.

5.3.1. Conical bullion

5.3.1.1. Characterisation

The unique lead bullion find (OB S003) was distinguished by its higher density and its long conical shape (Fig. 5.29). Its surface presents a smooth dark green layer of corrosion products, with yellow areas of ceramic residues adhering to it. The peculiar shape of this piece indicates that it did not solidify inside a crucible like those described before – a matter discussed later.

Fig. 5.29. *Conical lead bullion piece (OB S003; scale bar 5 cm; photo: A. Mongiatti).*

The bulk composition of this artefact shows a high concentration of lead (62 wt% Pb), with high amounts of antimony (25 wt% Sb), and some silver (8 wt% Ag), copper (3 wt% Cu) and arsenic (2 wt% As). This cone is composed of a matrix of metallic lead with numerous inclusions of speiss, mostly silver antimonide (Ag_3Sb) and copper arsenide (Cu_5As_2), and of matte (Fig. 5.30). The latter are either pure lead sulphide or a binary system of copper and lead sulphides.

At the very top, a thin layer of this particular matte, composed of dendrites of lead sulphide and interdendritic copper sulphide, is sitting on the main lead matrix, which has now corroded into cerussite, recognisable from its dull grey colour (Fig. 5.30-5.31). This observation indicates that initially a thicker matte layer was sitting on top of this lead bullion, rather than a slag layer. This is consistent with the three-layer system argued for so far.

Some ceramic attached to the cone was removed from the surface during the sampling. This ceramic is mainly composed of silica (75 wt% SiO_2), mostly due to a

large quantity of quartz grains; some alumina (10 wt% Al_2O_3), lead oxide contamination (6 wt% PbO), iron oxide (5 wt % FeO), and lower amounts of potash and soda. This may be informative about the composition of the vessel in which this bullion was produced – a matter that will be discussed below.

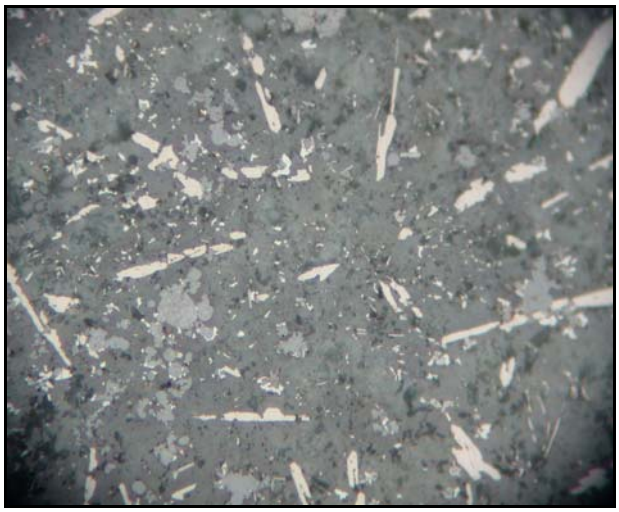


Fig. 5.30. *Microstructure of cone OB S003: lead carbonate (dull grey matrix), silver antimonide (acicular bright crystals), and copper and lead sulphides (light grey inclusions) (OB S003/S1, optical microscope in plane polarised light, 500x, long axis ~250 µm).*

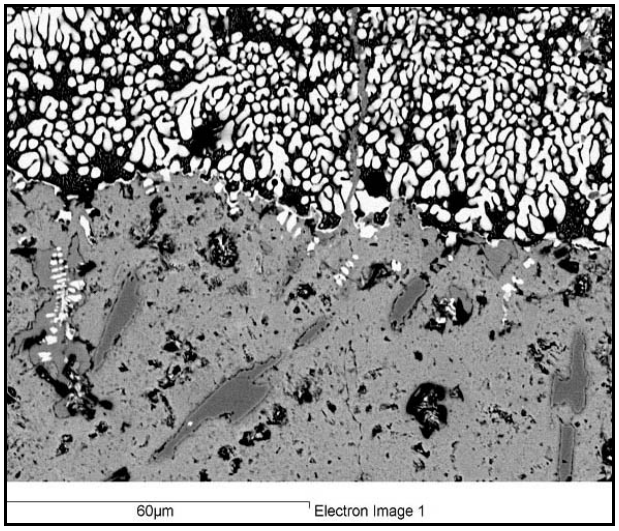


Fig. 5.31. *Matte (bright lead sulphide and very dark copper sulphide) on top of a corroded lead matrix (light grey); silver antimonide crystals in darker grey (OB S003/S1, BSE, 1000x).*

5.3.1.2. Discussion

The results of the analyses of the piece of conical lead bullion are consistent with the interpretation that this find originates from the testing of an antimony- and copper-bearing material for its content in silver; this material being an ore, as established above. This artefact also corroborates the use of lead metal as noble metal collector in the charge, though, as seen earlier, it has to be borne in mind that some of the lead could originate from the ore. As noted above, several fragments of thin sheets of lead metal have also been found as part of this archaeological

assemblage; this would have the ideal form for lead to be added to the charge in the triangular crucibles. It has to be noted that these lead sheets would also have been used for cupellation (see below). Besides, as explained in chapter 4, silver-free lead is in most cases the unanimously recommended collector for noble metals.

The conical shape of this object indicates that it did not solidify in a flat-bottomed triangular crucible. The ore fusion may still have been performed in a triangular crucible, the content of which could have then been poured into a different container to be left to cool outside the furnace. Descriptions of conical vessels can be found in written sources, especially in Agricola's and Ercker's treatises (Fig 5.32), where these are said to be made out of brass or iron and used in a very specific context, which is the parting of gold and silver with antimony sulphide (Hoover and Hoover 1950: 451-3; Sisco and Smith 1951: 195-7). The products of this latter procedure would have been an antimony-gold alloy and silver sulphide (Ag_2S). Thus, it appears that the lead-rich conical bullion found in Oberstockstall is definitely not the product of this parting technique, though it may have formed in a similar vessel.

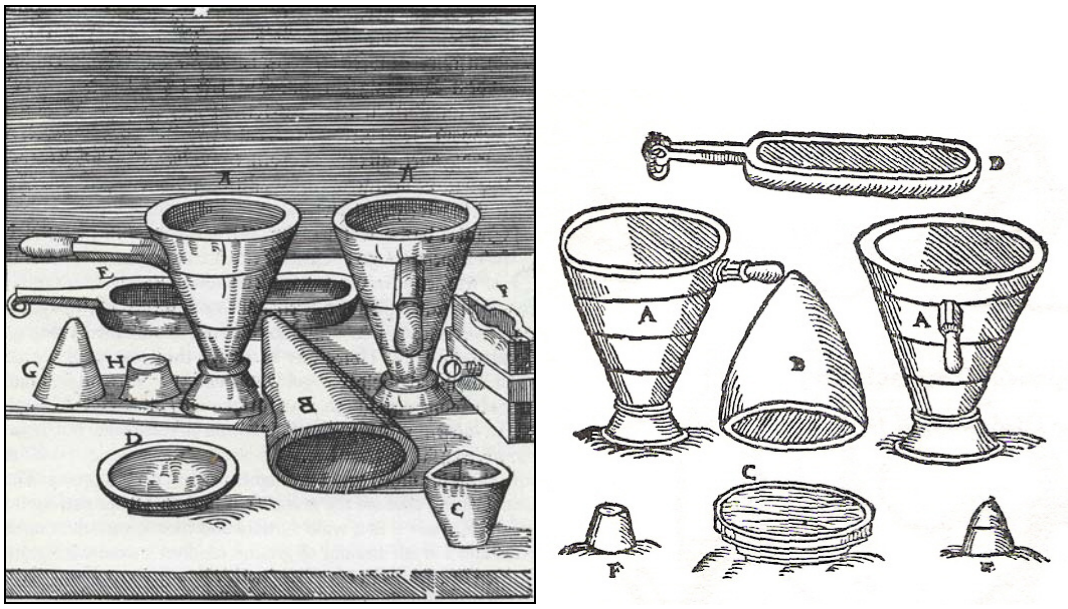


Fig. 5.32. *Conical vessels cast in brass or iron used in gold-silver parting with antimony sulphide after Ercker (left) and Libavius (right) (letter A) (left: after Sisco and Smith 1951: 197; right, after Atterer* et al. *1964: Bildteil 54).*

This metallic cone does not find its crucible counterpart in the assemblage. The vessel in which it solidified was ceramic, as shown by the areas on its surface where

this material is still attached. Archaeological examples of such conical vessels made of ceramic are known from Hesse (Stephan 1995). It has to be highlighted that almost all the used triangular crucibles from Oberstockstall were still in one piece when thrown away and do not seem to have been intentionally broken to remove the solidified content; the damage of some fragmented ones appears to have taken place after discard. Besides, many of the crucibles, which show traces of use at high temperature, appear to have residues from pouring on at least one of their three mouths (Fig. 5.33). It seems therefore reasonable to assume that the melt was usually not left to cool in these crucibles, but to argue instead that conical ceramic moulds may have been used as receptacles of the melted charge, and that these were broken after cooling to recover and separate the three layers of metal, matte and slag. This shape, narrowing towards the bottom, would have helped their separation. The fragments of the broken conical moulds would have been discarded together with the other waste of the laboratory, separate from the better-preserved crucibles which were initially kept in the laboratory. This aspect, i.e. the extent to which the assemblage recovered represents all the equipment and materials available at the laboratory, will be discussed more fully in the general discussion (cf. chapter 7).

Fig. 5.33. *Triangular crucible showing characteristic traces of pouring: the melt partly ran down the outer surface of the crucible wall during the pouring operation (scale bar 5 cm; photo: M. Martinón-Torres).*

5.3.2. Matte cakes and fragments

5.3.2.1. Characterisation

- **Morphological study**

Some of the matte cakes still have the original shape of the vessel in which they were produced and solidified, or show at least one surface which was laying against the inner wall of the vessel. The matte cake OB S001 has the diagnostic triangular shape of the upper part of a medium-sized crucible (Fig. 5.7 p.116, 5.34). OB S002 has a circular shape, which could be linked to the lower rounded section of a relatively big triangular crucible (Fig. 5.35). Three further matte fragments exhibit original surfaces. This surface is usually characteristic of a circular outline (Fig. 5.36) similar to OB S002, possibly indicating that these pieces of matte were situated at a relatively low height in a triangular crucible. As discussed in detail above with the interpretation of the results obtained on the bullion find, one possibility for this circular shape could be that the melt was poured into and left to cool in a different receptacle whose inner section was rounded. The triangular section of one matte – and possibly the rounder one of the others – would indicate, on the other hand, that the three layers of metal, matte and slag were left to cool inside the triangular crucibles. From the current evidence, it may be suggested that both cooling procedures may have actually taken place.

Fig. 5.34. *Top view of a triangular shaped matte cake (OB S001, scale bar 5 cm; photo: A. Mongiatti).*

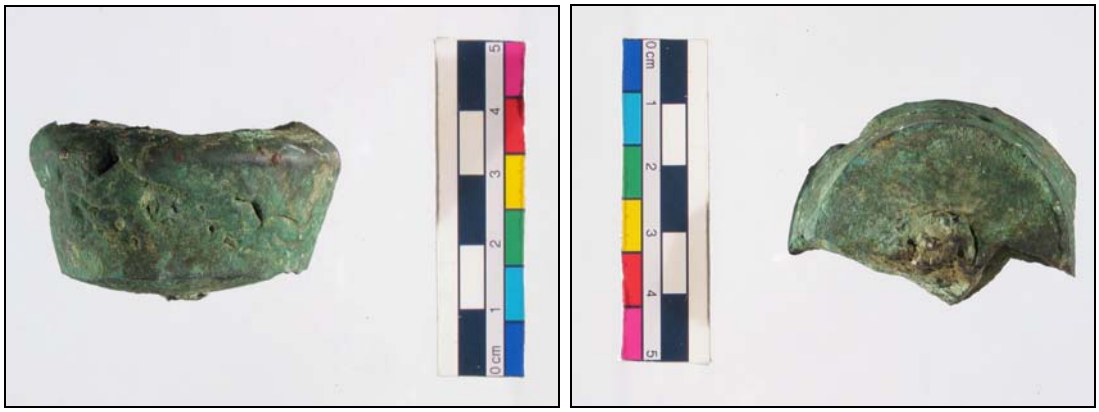


Fig. 5.35. *Round shaped matte cake with rims substantiating the existence of two layers of different densities above and below (left: side view of outer rim; right: bottom view; OB S002, scale bar 5 cm; photos: A. Mongiatti).*

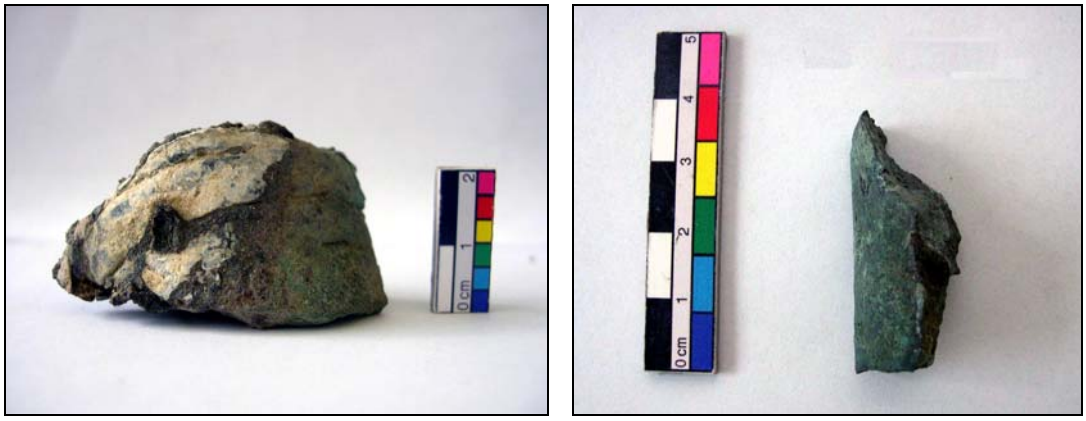


Fig. 5.36. *Examples of two matte cakes exhibiting a rim: note the circular shape preserving the inner section of the vessel in which they solidified (left: OB S005, scale bar 2 cm; right: OB S005, scale bar 5 cm; photos: A. Mongiatti).*

When visible, another interesting macroscopical feature of these sulphidic products is their rim. The shape and orientation of the upper and lower rims seems to indicate that they were sitting on a denser material whilst a lighter material was on top of them. The best illustration of this phenomenon is sample OB S002, where one can clearly see the particular shape of the meniscus of the lower surface (Fig. 5.35). This is consistent with the metal-matte-slag layered arrangement identified in the crucibles.

The estimated density of these matte fragments is roughly around 5, making them a lot less dense than a lead-rich cake, whose density would be around 11. They are usually not very porous, except for a few large pores on their upper surface. Their outer aspect is very variable, looking smooth and relatively homogeneous for some samples, while very heterogeneous and disturbed for others. They are covered

by superficial corrosion products of various colours, such as green, black, and/or yellowish, which are mainly a sign of the presence of copper in the sample. Other matte pieces have large rusty areas, indicative of iron. One side of the lump OB S001 exhibits a dark grey, shiny layer, seemingly of graphite-rich ceramic, as typical for the crucibles in Oberstockstall (Martinón-Torres *et al.* 2003; Martinón-Torres 2005).

- **Microstructural and analytical study**

The freshly cut inner surfaces have a dark grey, relatively shiny and porous texture, contrary to the first macroscopical approach. Their microstructural and chemical analyses indicate a complex sulphur-dominated system, clearly identifying them as matte fragments, as opposed to the oxide-based slag. Four of these six matte fragments have a similar bulk composition, with a major contribution from iron (32 to 35 wt% Fe), high concentrations of copper (19 to 23 wt% Cu), and lower amounts of lead (8 to 11 wt% Pb) and antimony (1 to 4 wt% Sb) (Table 5.6). These elements are distributed between newly-grown and distinct sulphidic phases, mainly large crystals of pyrrhotite; a mixture of chalcopyrite ($CuFeS_2$) and a complex copper and iron sulphide of bornitic composition (bornite Cu_5FeS_4), which has formed during cooling from the disintegration of a high-temperature metastable sulphide of copper and iron (51 wt% Cu, 19 wt% Fe, 30 wt% S); and galena. The lead sulphide is often found with the copper-iron sulphide system as a eutectic mixture (Fig 5.37). Part of the bornite has now corroded away and been replaced by post-depositional blue covelline, which has filled most of the phase boundaries.

	O	Al	Si	S	K	Ca	Fe	Cu	Sn	Sb	Pb
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
OB S001/S1	10.1	0.7	1.7	14.3	0.8	0.8	8.0	17.5	b.d.l.	19.3	26.7
OB S002/S1	7.7	b.d.l.	b.d.l.	22.5	b.d.l.	b.d.l.	35.2	23.3	b.d.l.	1.6	9.6
OB S005/S1	15.2	0.2	0.6	21.4	b.d.l.	b.d.l.	33.1	19.4	b.d.l.	2.5	7.6
OB S007/S1	11.2	b.d.l.	0.3	21.6	b.d.l.	0.2	31.7	20.1	b.d.l.	3.8	11.1
OB S008/S1	8.6	b.d.l.	b.d.l.	23.3	b.d.l.	b.d.l.	33.5	23.4	0.8	1.4	9.0
OB S009/S1	3.2	b.d.l.	b.d.l.	15.1	b.d.l.	b.d.l.	1.4	17.4	b.d.l.	21.6	41.3

Table 5.6. *Average chemical composition by SEM-EDS, normalised to 100 wt%, of the bulk of the matte fragments (area analysis at magnification 100x) (b.d.l.: below detection limit).*

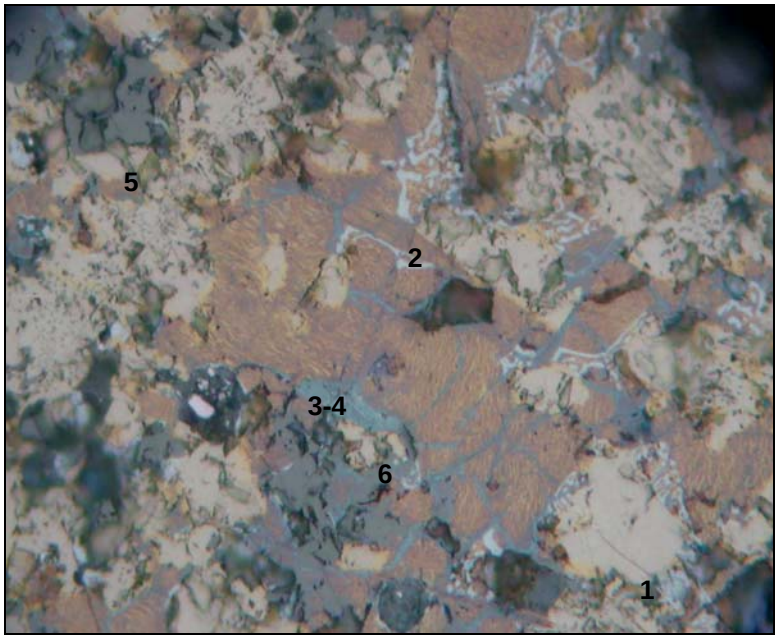


Fig. 5.37. *Microstructure of a matte fragment: main phase of pyrrhotite (cream-coloured, 1); eutectic mixture of lead sulphide (white, 2) with the phases of chalcopyrite (yellow, 3) and bornite-like complex copper-iron sulphide (brown-flesh coloured, 4); iron oxide (grey, 5); and zones filled by secondary covelline (blue, 6) (OB S002/S1, optical microscope, plane polarised light, 1000x, long axis ~120 µm*).

These samples exhibit signs of oxidation (8 to 15 wt% O), mostly in the form of numerous magnetite crystals forming from the hot oxidation of pyrrhotite. They also include prills of antimony, usually associated with lead and/or copper, and partially corroded for most of them. In some samples, the analyses show locally high levels of tin (10 wt% Sn, OB S005/S1, OB S007/S1) and bismuth (12 wt% Bi, OB S007/S1) associated with antimony. Phases of speiss composed of copper and iron antimonides (Cu_2Sb, $FeSb_2$) are also detected in the metallic inclusions of most of the specimens. There are several large round phases of pure lead sulphate, which were probably originally lead metal that has corroded away. These sulphates are not likely to have been sulphides initially, since sulphidic phases would not form separate prills, but would rather be integrated in the sulphur-rich system described above, and form eutectic mixtures with the copper-iron sulphide as previously mentioned.

The other two matte pieces – OB S001 and OB S009 – are much poorer in iron and the main constituting elements are lead, antimony and copper.

The microstructure of the former is comprised of bournonite ($CuPbSbS_3$), galena and a complex copper-antimony-iron sulphide, which is a type of iron tetrahedrite

($(Cu, Fe)_{12}Sb_4S_{13}$) (Fig. 5.38). The latter two compounds are locally found as a eutectic mixture, which has started to corrode in some areas. Selective weathering of the lead sulphide can be seen, leaving voids filled by secondary post-depositional blue covelline (CuS), while the other sulphides remain stable. The analyses also reveal several prills of antimony metal (99 wt% Sb, OB S001/S3), recognisable from their typical corrosion in lines crossing the inclusions (Fig. 5.13, p. 125 and Fig. 5.40). One spot analysis has also revealed the presence of silver (1.8 wt% Ag) in a copper-rich sulphate phase (41.7 wt% Cu, 11.0 wt% Sb, 9.0 wt% Pb, 0.7 wt% Si, 20.5 wt% S, 15.3 wt% O) at grain boundaries, in the sample from the top surface (OB S001/S1, SEM-EDS).

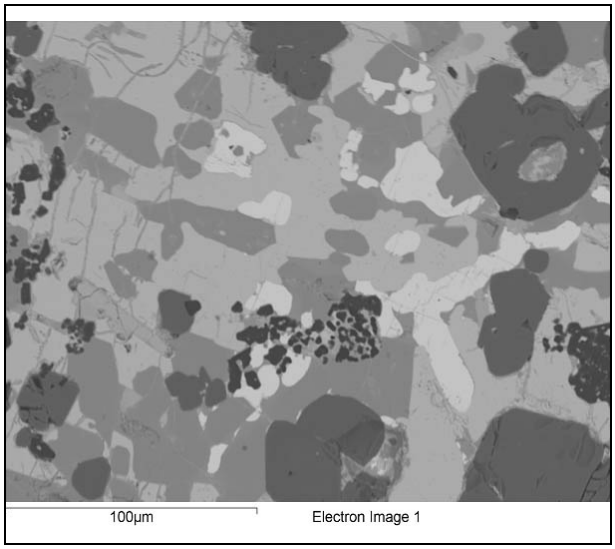


Fig. 5.38. *Microstructure of the upper section of the matte cake OB S001: galena (white), bournonite (light grey) and tetrahedrite (medium grey); magnetite (large dark grey crystals) and calcium-iron silicate-rich phase (small darker grey crystals) (OB S001/S1, BSE, 500x).*

One of the two specimens removed from the upper surface (OB S001/S2) has a lot more of the eutectic mixture of lead sulphide/tetrahedrite, implying a gradient in the cooling rate at the same horizontal level in the crucible (Fig. 5.39). The sample removed from the lower surface (OB S001/S3) is mainly composed of large and well-developed dendrites of tetrahedrite, in which small phases of galena have grown. Both these phases formed from a metastable complex compound, which upon cooling separated into the main phase of tetrahedrite and the small crystals of galena (Fig. 5.40). This difference in the size of the phases, which are larger at the bottom of the sample, suggest a vertical gradient in the cooling rate in the crucible, the top cooling much more quickly than the bottom, as the melt, which produced this particular triangular matte, was left to cool in the reaction vessel itself. This could be

explained by the fact that the matte in the crucible sits on top of the metal, which has a high thermal capacity and hence keeps the lower part of the matte hot for longer.

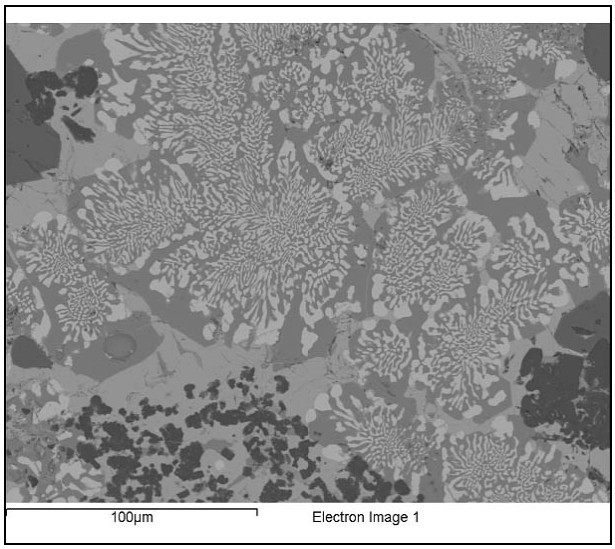


Fig. 5.39. *Eutectic mixtures of galena (bright) and tetrahedrite (medium grey), with some bournonite (light grey), magnetite (dark grey) and slag inclusions (black) on the upper surface of OB S001 (OB S001/S2, BSE, 500x).*

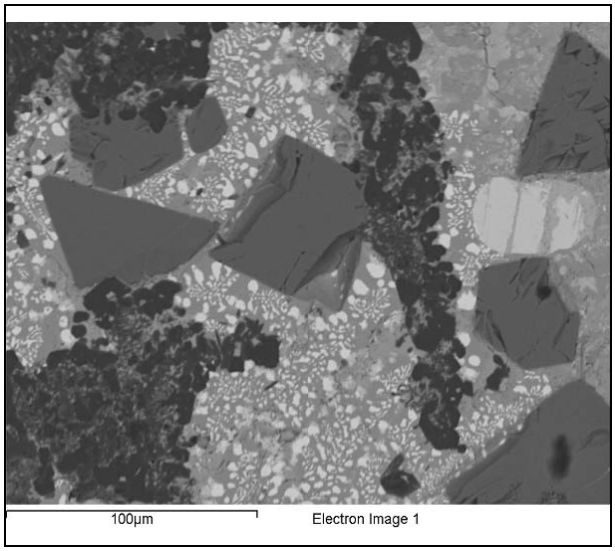


Fig. 5.40. *Microstructure of the lower side of OB S001: large phases of tetrahedrite (pale grey) with small included crystals of galena (bright); large cubic magnetite crystals (dark grey) and areas of small slag inclusions (black). Note the bright partially corroded prill of antimony metal on the right (OB S001/S3, BSE, 500x).*

The matte piece OB S009 is characterised by the presence of large dendrites of lead sulphide with an interdendritic eutectic mixture of lead sulphide and tetrahedrite. Some blue covelline can be noticed in numerous tiny zones, which is probably a product of the corrosion of the copper-rich tetrahedrite phase. There is a gradient in the size of the dendrites, showing a cooling gradient from one side of the sample to the other (Fig. 5.41). This could be due to one surface being closer to the open top of the vessel in which it was left to solidify, similarly to sample OB S001, or one side of this same container became cooler more quickly than the other side, maybe standing in front of the hearth of the furnace. The dendrites are organised into

a spinifex structure, all growing perpendicularly to one surface, which seems to have been the cooling front. Relatively small prills of antimony, some highly corroded and others still mostly metallic, are distributed evenly across the sample. One side exhibits a superficial layer, clearly separate from the main body of this sample (Fig. 5.42). The analysis of this dark grey layer revealed an iron oxide-rich phase (64 wt% FeO) with significant amounts of silica (9 wt% SiO_2), copper oxide (10 wt% CuO), antimony oxide (9 wt% Sb_2O_3), lead oxide (4 wt% PbO), and lower quantities of lime (2 wt% CaO), sulphur (1 wt% SO_2), and phosphates (1 wt% P_2O_5).

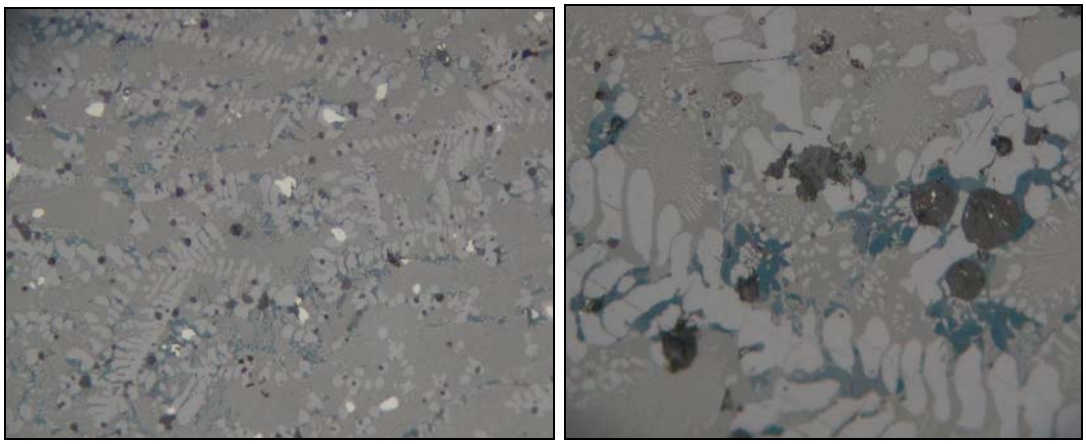


Fig. 5.41. *Pale dendrites of lead sulphide showing a clear size gradient. Note the prills of antimony, bright metallic on the left, corroded and grey on the right. (OB S009/S1, optical microscope, plane polarised light, both 500x, long axis ~200 µm).*

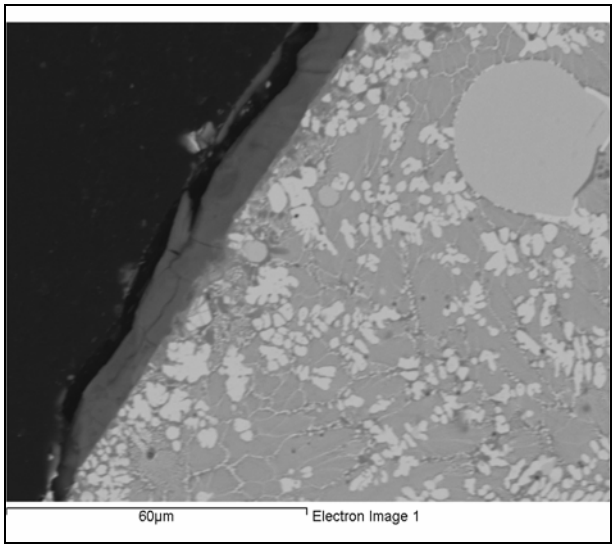


Fig. 5.42. *Iron oxide-rich layer (left) showing a neat interface with the matte (OB S009/S1, BSE, 1000x).*

The oxygen-rich part of the system of the matte cakes also varies between the four iron-rich specimens and the other two. In the former, the phases identified were large crystals of magnetite, which account for most of the oxygen detected in the

bulks. Two of these four samples also have occasional large slag inclusions, which are rich in silica, iron oxide, calcium oxide, alumina, potash and soda. The iron within these slag phases is mainly present in abundant crystals of magnetite within a silicate glass (Fig. 5.43). The composition of the glass of these slag particles is reminiscent of that of analysed crucible slag remains.

On the other hand, the triangular matte OB S001 exhibits many silicate crystals of various sizes but always smaller than the well-developed sulphides, which are rich in calcium-iron silicates (pyroxenes) or potassium-iron silicates. The latter are feldspathoids similar to leucite ($KAlSi_2O_6$) and typical of a silica-poor environment. Comparable slag inclusions were also identified in matte sample OB S009.

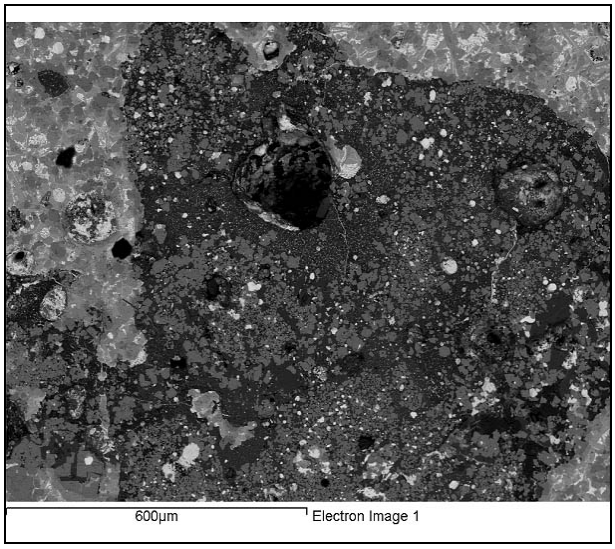


Fig. 5.43. *Large slag inclusion within a matte cake, composed of a silicate glass enriched in CaO, Al_2O_3, K_2O, Na_2O, FeO with numerous magnetite crystals and antimony prills (OB S001/S3, BSE, 500x).*

5.3.2.2. Discussion

- **Matte: a product from the reducing crucible fusion of a sulphidic ore**

The matte cakes almost certainly have their origin in the triangular crucibles. This is inferred from their microstructure and chemical composition, and by the typical triangular shape of OB S001, which links it directly to this kind of vessel, although most of these fragments present a circular section. Their elemental composition relates them further to the triangular crucibles and their internally attached high-temperature waste products in many ways. First, they find their direct equivalent in the crucible matte sample OB 519B/S1, whose main phase is tetrahedrite, and in the sulphidic inclusions of many crucible slag samples. Furthermore, the high iron levels in most of the matte pieces are also identified in the

slag, enriching the glass and forming discrete magnetite crystals. As with the crucible slag remains, the origin for the large amounts of iron in the matte cakes could be the ore itself, since gold and silver often occur in pyrite; or a flux deliberately added to the crucible charge. As seen earlier, this iron-rich additive may either be metal filings or pyrite, as listed by Agricola amongst his fluxes (Hoover and Hoover 1950: 234). This high iron content of the various matte fragments is also to be related to the scorifier slag layers. The latter display the same characteristic, which suggests that matte was occasionally a potential raw material for scorification (see below).

The high amounts of lead, antimony and copper (Table 5.6, p. 154) support the previous hypothesis of the reducing fusion of a complex sulphidic ore, such as tetrahedrite, or of a complex mixture of iron-rich sulphidic ores, combining, for instance, pyrite, chalcopyrite, arsenopyrite, etc. The incidence of these pieces of matte in the assemblage from Oberstockstall and the study of their morphology and microstructure confirm the development of the three layers of metal, matte and slag in the crucibles.

Similarly to the matte inclusions of the crucible slag layers, some discrete globules of slag remained trapped in the pieces of matte. This may be a consequence of a fast cooling or a high viscosity of the phases, which hindered the diffusion and complete separation of the metallic, sulphidic and oxidic phases. As established before, these slag inclusions in the matte cakes show significant concentrations of iron oxide, calcium oxide, potash, and soda. This enrichment is very similar to the crucible slag samples analysed, once again relating the formation of these matte fragments to the triangular crucibles. The numerous antimony prills identified in these matte finds, within the sulphidic system as well as in the slag inclusions, link them further to the triangular crucibles. The recurrence of antimony, bismuth, copper and silver in these prills corroborates the possible treatment at high temperature of a fahlore, rich in these various elements, for its content in silver.

One difference between the slag residues and the various matte remains is the high antimony content of the latter. The concentration of antimony was much lower in most of the slag layers of the crucibles and, as will be seen later, the scorifiers, only noticed as a few corroded particles. Most of the antimony would be collected in the lead-rich metallic phase, as shown by the conical lead bullion for instance. However, the great affinity of antimony for sulphur and for metals such as lead,

silver, and copper would explain why there is normally an antimony-rich matte and an antimony-poor slag. This high amount of antimony and the identification of silver strengthen the argument suggested above, that is the test of a complex sulphidic ore for its content in precious metals, this ore being probably rich in antimony. This also suggests that the antimony-rich matte finds and the iron-rich matte cakes are, respectively, the products of the processing of different ores.

- **Matte: a unexpected product**

Matte is usually undesired in fire assay, as it retains some of the noble metals, which are then lost for the lead bullion, potentially leading to a bias in the quantification of the noble metals contained in the ore sample. This sulphur-rich material seems to have been kept by the chymist(s) of Oberstockstall and further refined by successive scorifications; the ultimate scorifier bullion produced by a series of these oxidising reactions being finally cupelled. This would have allowed the extraction of the noble metals from matte and determine more precisely their proportions in the original ore sample assayed. As mentioned above, the occurrence of these matte cakes in the archaeological record at Oberstockstall together with some of the residues analysed and all the necessary tools and equipment indicates that they may have been kept for such a treatment in the context of recovering the silver from them or to study their properties in a research context. This hypothesis of the scorification of matte is explored in detail in the next section, which concerns the scorifiers, and would further emphasise the research character of this Renaissance laboratory.

A relatively easy way of avoiding the formation of matte is roasting the ore in oxidising conditions in order to drive off the sulphur prior to the reducing fusion. This was the procedure advised by sixteenth-century writers (Hoover and Hoover 1950: 242; Sisco and Smith 1951: 114) but was not carried out here. However, because matte is not meant to be part of the expected products, the various Renaissance authors make almost no suggestion regarding its further refining in the case of ores containing precious metals; except for some explanations in Ercker's text on how to assay copper matte for its silver or copper content (Sisco and Smith 1951: 46-48, 218). Ercker's position seems to stand out from his two contemporaries; he advises adding antimony sulphide with litharge and iron filings if the ore does not contain any iron to the ore when starting a fire assay in a triangular

crucible, and then scorifying the lead bullion and the slag together (Sisco and Smith 1951: 112-114). This would probably require more than one scorification. Despite this potential source for sulphur and antimony being different from the ore, the thickness of the matte cakes analysed here and the richness of the ore – or mixture of ores – in these two elements suggest that these matte cakes most likely resulted from the melting of a sulphidic ore. Besides, the absence of antimony in the processed arsenic-rich ore sample seems to further substantiate this argument. However, if some antimony sulphide had been added to this antimony-rich sulphidic ore, the analytical data would not allow us to determine it.

5.3.3. Summary on the matte and bullion finds

The detailed study of the various isolated matte cakes and fragments has shown that they were produced in the triangular crucibles, through the reducing fusion of a sulphidic ore, resulting in the formation of three layers of metal, matte and slag in these reaction vessels. The existence of such material in the archaeological assemblage suggests that the ore was not roasted before being processed in the triangular crucibles, which is different from what is typically advised in metallurgical texts of the sixteenth century. The archaeological context also implies that the matte cakes were not discarded but kept for possible additional treatment to assess their noble metal content, which constitutes part of the trapped metallic prills of antimony and lead, or test their chemical properties. The matte cakes could then either be scorified, in a similar way to the lead-rich bullion products, as will be shown in the next section, or further processed to study this particular material.

5.4. Scorifiers remains

As previously described in the initial section of this chapter, scorifiers are open shallow ceramic dishes probably used in oxidising reactions of various kinds. Used scorifiers typically show a slag layer placed around a central depression (Fig. 5.44).

Fig. 5.44. *Top view of a used scorifier, showing a yellow layer of slag with a central depression (scale bar 5 cm; photo: M. Martinón-Torres).*

5.4.1. Characterisation

5.4.1.1. Slag phases

The scorifier slag residues were prepared as polished thick cross-sections of both the ceramic and the metallurgical products, similarly to the crucible slag samples and the matte fragments. Eight of the studied scorifiers are made of a quartz- and alumina-rich clay, while five of them (OB 270, OB, 271, OB 279, OB 284, OB N006/S1) have a graphitic ceramic fabric. Their metallurgical residues are bright and glassy, with variable porosities and very different colours, from black or dark red to bright yellow or orange. Some specimens show that the slag has penetrated into pores or cracks of the ceramic, while others exhibit a neater interface with the ceramic. The thickness of this slag film varies from *ca.* 1 mm to *ca.* 3 mm (Fig. 5.45). The presence of the central depression within used scorifiers (Fig. 5.44) and the characteristic concave shape of most scorifier slag residues is indicative of the previous existence of some denser material attached to it, further to the centre of the scorifier (Fig. 5.44, 5.45 right).

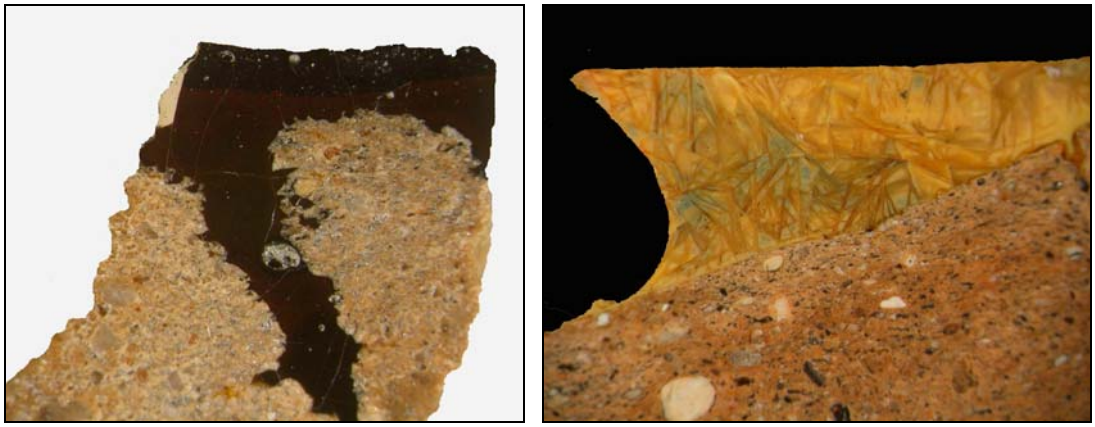


Fig. 5.45. *Examples of two macroscopically different scorifier slag layers (left: dark red and black; right: bright yellow) on top of the ceramic (light orange). Compare the crack where the slag has penetrated (left) and the very neat interface (right). Note the concave shape of the slag on the right, showing the central depression where a lead bullion was originally situated. Images from the stereoscopic microscope (left: OB 268/S1; right: OB 269/S1; 16x, long axis ~11 mm).*

Most of the glassy matrices of these slag remains are usually dense and homogeneous, clearly different from the crucible slag residues. They are typically composed of lead silicate, with a silica content ranging from 8 to 21 wt%, and some alumina (1 to 5 wt% Al_2O_3). Part of these slag remains are also enriched in iron oxide (1 to 11 wt% FeO), copper oxide (0.2 to 4 wt% CuO), lime (0.1 to 3 wt% CaO), and potash (0.2 to 1 wt% K_2O). Several lead-silicate glass matrices display relatively high levels of antimony oxide (5.8 to 6.1 wt% Sb_2O_3) and/or arsenic (0.1 to 8.5 wt% As_2O_3) (Table 5.8). These chemical data will be discussed below.

	Na_2O wt%	MgO wt%	Al_2O_3 wt%	SiO_2 wt%	K_2O wt%	P_2O_5 wt%	CaO wt%	TiO_2 wt%	FeO wt%	CuO wt%	As_2O_3 wt%	Sb_2O_3 wt%	PbO wt%
OB 268/S1	b.d.l.	b.d.l.	5.0	17.2	0.5	b.d.l.	0.9	b.d.l.	5.4	0.8	b.d.l.	b.d.l.	70.3
OB 269/S1	b.d.l.	b.d.l.	2.5	8.2	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	89.4
OB 270/S1	b.d.l.	0.3	2.4	9.6	b.d.l.	b.d.l.	0.1	b.d.l.	10.6	1.5	0.1	b.d.l.	75.4
OB 271/S1	b.d.l.	b.d.l.	1.0	2.9	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	92.0	4.1
OB 273/S1	b.d.l.	b.d.l.	5.9	20.9	0.5	b.d.l.	0.5	0.4	1.0	0.8	0.6	b.d.l.	69.5
OB 274/S1	b.d.l.	b.d.l.	3.2	11.1	0.5	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.2	b.d.l.	b.d.l.	85.0
OB 276/S1	b.d.l.	b.d.l.	4.8	16.5	b.d.l.	b.d.l.	0.1	b.d.l.	2.2	b.d.l.	b.d.l.	b.d.l.	76.4
OB 277/S1	b.d.l.	b.d.l.	4.4	16.9	b.d.l.	b.d.l.	b.d.l.	b.d.l.	2.1	3.0	b.d.l.	b.d.l.	73.6
OB 279/S1	b.d.l.	b.d.l.	2.8	9.7	0.5	b.d.l.	0.7	b.d.l.	1.7	b.d.l.	8.5	b.d.l.	76.1
OB 282/S1	b.d.l.	b.d.l.	5.0	20.4	1.3	b.d.l.	0.7	b.d.l.	5.4	b.d.l.	b.d.l.	b.d.l.	67.2
OB 284/S1	b.d.l.	b.d.l.	2.0	6.4	b.d.l.	b.d.l.	1.3	b.d.l.	5.3	b.d.l.	1.4	65.6	18.1
OB N006/S1	b.d.l.	0.9	4.6	13.8	0.2	b.d.l.	2.3	0.1	2.0	4.1	b.d.l.	b.d.l.	71.9
Average of ceramic matrices*	0.4	0.6	30.5	59.7	2.7	0.3	0.9	0.7	4.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.

***** after Martinón-Torres and Rehren 2005b

Table 5.7. *Average chemical composition by SEM-EDS, normalised to 100 wt%, of the matrices of the scorifier slag samples (b.d.l.: below detection limit). See appendix 3 for the full results.*

Many samples display discrete cubic phases of newly formed magnetite (OB 268/S1, OB 276/S1, OB 282/S1), and separate crystals of various feldspathoids, which have compositions similar to leucite ($KAlSi_2O_6$; OB 279/S1), kalsilite ($KAlSiO_4$; OB 276/S1, OB 279/S1, OB N006/S1) or lazurite ($Na_3Ca(Al_3Si_3O_{12})S$; OB 270/S1, OB 276/S1, OB N006/S1).

In the case of scorifier OB 268, the density of the magnetite crystals increases from the interface slag/ceramic towards the surface of the slag, where the conditions were certainly more oxidising. These oxidising conditions are confirmed by the great amount of platy crystals of a complex iron- and lead-rich oxide ($PbFe_{12}O_{19}$; 56 wt% Fe, 21 wt% Pb), where the iron is in its highest oxidation state (Fe^{3+}) and which are not detected deeper in the slag (Fig. 5.46). This local abundance of platy iron-rich crystals is probably due to a contamination by tongs during the manipulation of the scorifier, or by the iron hook or rod used to stir the charge in the scorifier. This iron rod would superficially oxidise in the hot furnace and in contact with the melt, and contaminate it locally with iron oxide. If the melt was stirred thoroughly with this iron bar as advised by Agricola and Ercker (Hoover and Hoover 1950: 242; Sisco and Smith 1951: 39, 112), then the contamination would be seen as an increase in the total iron concentration in the glass.

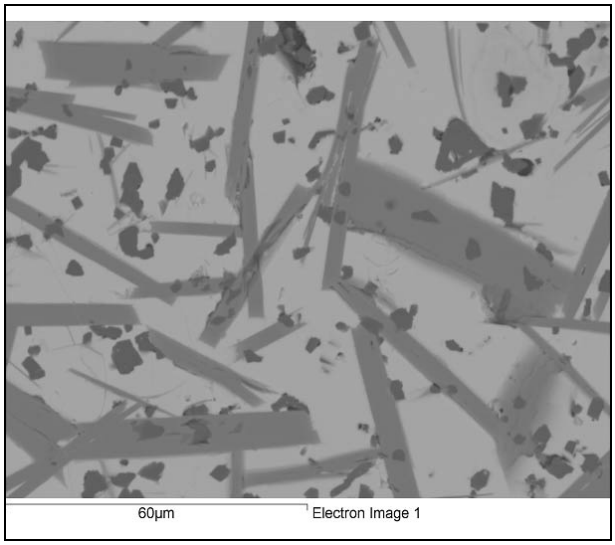


Fig. 5.46. *Area of the black slag close to the surface: light grey lead silicate glass, dark grey cubic magnetite crystals and platy medium grey crystals with a high amount of lead-containing iron oxide (OB 268/S1, BSE, 1000x).*

Few dispersed separate sulphidic matte inclusions were found in two scorifier slag samples. In one case, they are sporadic, large (*ca.* 100 µm), rounded and consist of distinct phases of mixed copper and lead sulphides (Fig. 5.47; OB 268/S1), while in the other instance, these inclusions are very small (*ca.* 5 µm) but abundant and mainly composed of a sulphide of lead (57 wt% Pb), copper (23 wt% Cu) and silver (4 wt% Ag) (OB 279/S1). Two samples display metallic prills, one having numerous small (*ca.* 10 µm) inclusions of copper metal (Fig. 5.48; OB N006/S1) and the other having one area showing a cluster of separate phases of almost pure gold (99 wt% Au, 1 wt% Ag) (Fig. 5.49, OB 273/S1).

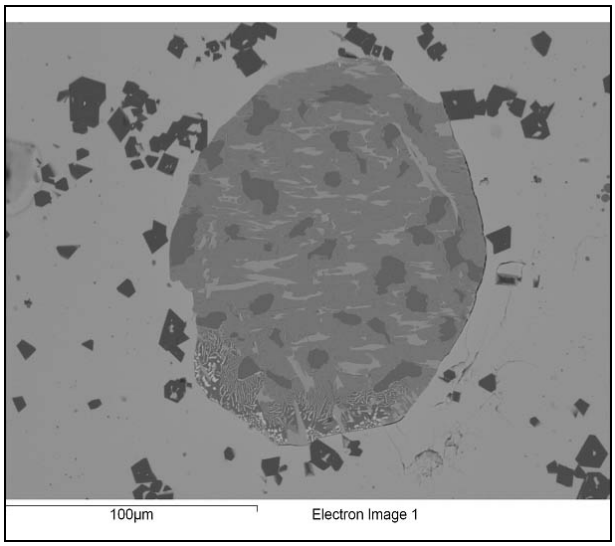


Fig. 5.47. *Complex inclusion of copper sulphide (medium dark grey) and lead sulphide (bright grey), with many magnetite crystals (dark grey) in a lead-silicate glass (light grey). The medium grey phase within the inclusion is an unresolved mixture of the two sulphides. (OB 268/S1, BSE, 500x).*

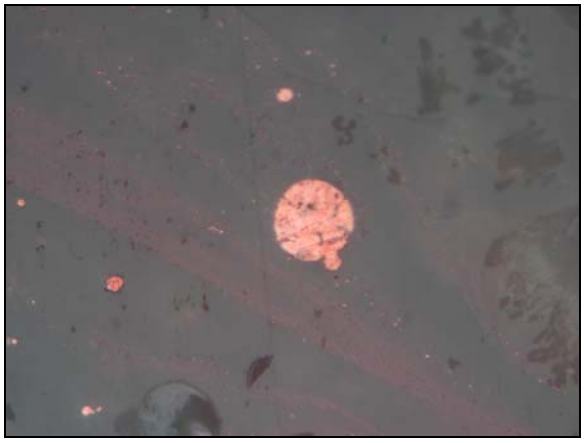


Fig. 5.48. *Bright orange prill of metallic copper (OB N006/S1, optical microscope, plane polarised light, 1000x, long axis ~150 µm).*

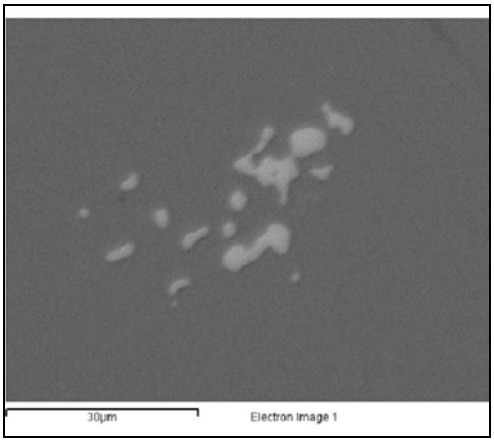


Fig. 5.49. *Light grey gold phases in a lead silicate glassy matrix (OB 273/S1, BSE, 1600x).*

5.4.1.2. Scorifier bullion remains

Scorification of crucible bullion, and possibly to some extent of crucible matte, would lead to the formation of scorifier bullion, which could potentially be scorified again as a further refining process and/or to reduce its size. Only one scorifier displays residues of a lead-dominated bullion that was produced by scorification, although the other scorifiers show indirect traces of bullions, such as the empty central depression over which the slag can be seen edging (Fig. 5.44-5.45). Scorifier OB 282 exhibits a layer of lead-rich material (86 wt% Pb), which contains a significant amount of silver (6 wt% Ag) and shows some traces of oxidation, probably due to exposure to oxygen of the air. This material attached to the slag most likely constitutes the remains of a bullion (Fig. 5.50). The metallographic study shows that it is composed of a grey lead-rich matrix, which has mostly corroded away into cerussite, with numerous separate bright white crystals of silver and orange phases of copper (Fig. 5.51).

Fig. 5.50. *Silver- and copper-rich lead bullion layer (bottom) attached to an homogeneous lead-silicate slag (top) (OB 282/S1, optical microscope, plane polarised light, 500x, long axis ~300 µm).*

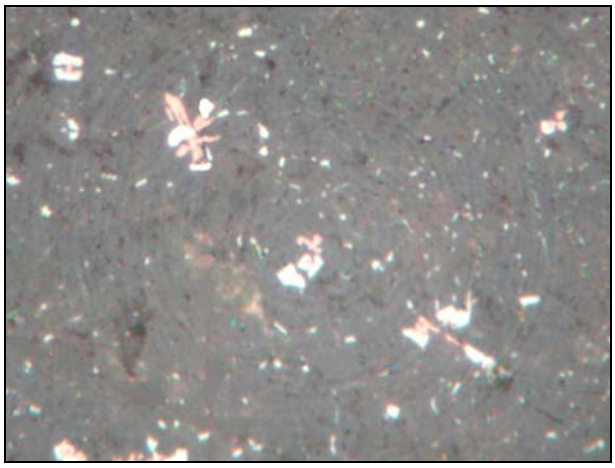


Fig. 5.51. *Matrix of lead carbonate (grey) with separate crystals of metallic copper (orange) and silver (white) (OB 282/S1, optical microscope, plane polarised light, 1000x, long axis ~150 µm).*

5.4.2. Discussion: a potentially wide utilisation of the scorifiers

From the analysis and metallographic study of these scorifier slag remains, it has been shown that they are primarily composed of a main lead silicate matrix, with separate silicate inclusions. The composition and microstructure of these slag residues attest to the oxidising conditions of the reactions performed in these vessels – conditions which could already be implied by the open shape of the scorifier itself.

The various separate phases of metal and matte inform about the materials treated in these ceramic reaction vessels. These were mostly pieces of bullion, usually contaminated with some matte still attached to it from the crucible fusion. As indicated by higher iron oxide concentration in several scorifier slag specimens, matte also produced during the previous step of the crucible fusion of a sulphidic ore was most likely occasionally scorified, as explained below. The aim of this oxidising stage would be to further refine the bullion prior to the final cupellation, by reducing its size and the amount of base metals, which would go into the scorifier slag. The generally high lead content of the slag may originate from the raw material, i.e. the

lead bullion to be scorified. In the few cases where matte seems to have been further refined, lead could be a contribution of the bullion, if both bullion and matte were scorified together, or it could come from the addition of silver-free lead. Lead is usually not recommended by sixteenth-century texts in the scorification following crucible fusion; it is, however, required when scorification is the first step of the fire assaying sequence (cf. chapter 4). It is indeed possible that the chymist in Oberstockstall treated his matte as he would an ore when applying the scorification-cupellation method (cf. chapter 4). The depression visible in the centre of many of the scorifiers is probably the impression left by the lead concentrate, rich in noble metals, which would be removed for further processing. The silver-rich oxidised lead bullion identified in scorifier OB 282 is most likely a residue of such material.

5.4.2.1. The principal utilisation of the scorifiers

The oxide-rich slag and traces of use on the scorifiers show that these vessels underwent a high-temperature process under oxidising conditions. According to Agricola and Ercker (Hoover and Hoover 1950: 241-242; Sisco and Smith 1951: 112-114), there are two potential scenarii here: one would be the scorification of an ore – if the procedure was starting with a scorification step –, and the other would be the scorification of a lead-rich bullion obtained via the previous reducing fusion in a triangular crucible. The two authors mentioned above advocate the use of the first sequence in the case of silver ores, and of both for gold ores (cf. chapter 4). In the laboratory practice of Oberstockstall, where the crucible fusion of ores has been documented, the latter procedure seems more likely to be the case.

In addition to this typical fire assay methodology the scorification of matte must, however, be considered as a further possibility. This latter material seems to have been relatively infrequently refined by scorification and then by cupellation, in order to determine its content in precious metal and therefore the loss of silver induced in this phase, or for wider research purposes. A careful look at the analytical data allows a more precise interpretation.

The composition of the slag residues in the scorifiers is less complex compared to the crucible slag remains, indicating that the raw materials were different. The

composition of the glass matrices also confirms that the substance scorified was not a raw ore: the slag is lacking of typical gangue and mineral components, such as titanium, magnesium, zinc and lime (Table 5.7, p. 165), except for one sample (OB 281/S1 slag 2), which is discussed separately below.

The high lead oxide concentration, which varies from 67 to 89 wt% PbO, with an average of *ca.* 75 wt% PbO, in the lead silicate glass, clearly indicates that the raw material scorified was a lead bullion. In scorifiers with a lead-dominated slag, the oxides of antimony and arsenic most likely originate from the crucible bullion, which had collected these metalloids from the fahlore during crucible fusion, or from some matte contamination through the presence of inclusions in the bulk or fragments stuck to its surface. For the few slag samples suspected to have formed from the scorification of matte – or matte and bullion together –, metallic lead was probably added to the scorifier charge to facilitate the collecting of the noble metals from the melt and the oxidation of the base metals, especially if scorifying matte on its own. For typical scorification, none of the three Renaissance authors recommends the addition of lead metal, since the aim of this operation, besides purifiying the bullion by removing the impurities into a slag, is to reduce its size prior to cupellation. The only reason for lead to be added to the scorifier would be if scorification was the first reaction of the fire assay, as described in chapter 4. The matte perhaps visually behaving similarly to the sulphidic minerals processed in this laboratory may have been treated in the same manner, i.e. scorified with fluxes and lead as collector.

During scorification, part of the lead would have oxidised and reacted with the fabric of the vessel, producing lead silicate slag containing various elements from the ceramic, such as alumina. The SiO_2/Al_2O_3 ratio of the slag residues ranges from 3 to 4, with an average of *ca.* 3.5, meaning this is higher than in the ceramic, where it almost reaches 2. This lower alumina proportion in the slag might be due to a selective melting of the quartz particles of the ceramic, or to the silica-rich impurities in the charge, such as slag inclusions. For the slag samples containing some iron, the SiO_2/FeO ratio ranges from *ca.* 1 to 21, with an average of *ca.* 7. Similarly for the slag remains in which calcium has been detected, the SiO_2/CaO ratio shows values between *ca.* 6 and 96, with an average of *ca.* 35 (Table 5.7, p. 165). This means that the slag is about twice as rich in iron and calcium oxides than it would be if it were originating from the underlying ceramic only.

It has been shown that bullions were not rich in iron and calcium, at least not enough to account for such an enrichment of the scorifier slag in these elements. One fairly straightforward explanation for the lower fraction (1-2 wt% FeO) of these relatively elevated quantities of iron and calcium could be the contamination of the lead bullion by some matte still attached to it or occurring as trapped inclusions in its bulk, and/or some contamination from the heavy stirring of the molten charge with an iron tool. In some cases, the level of these oxides seems however too high (5-10 wt% FeO) for such an origin and one could think that the chymists in Oberstockstall were scorifiying lead bullion and slag together. This could sound as a plausible justification for these higher concentrations, since Ercker actually advises to scorify both the bullion and the slag together (Sisco and Smith 1951: 112). If the crucible slag were rich in iron and calcium after the first fusion, then the slag formed by scorification would hold some of this characteristic. The easily oxidised iron would stay in the oxide-rich phase, not miscible with the metallic phase. However, it is very likely that the crucible slag was discarded after the processing of the ore in a triangular crucible, not least because the slag would not normally retain any noble metals, and therefore there would be little point in refining it. As mentioned above, a more convincing explanation would be that, instead of slag, matte was the material scorified jointly with the lead bullion. Indeed, the higher iron and calcium contents, together with the occurrence of copper in more than half of the samples, recall the matte cakes characterised earlier, part of which have a significant amount of iron oxide in the bulk (32 to 35 wt% Fe; Table 5.6, p. 154), and another displays numerous slag inclusions rich in calcium and iron oxides. With high temperatures, the sulphur would drive off, the iron quickly oxidise and go into the slag – therefore enriching it – while the calcium oxide phases would remain separate from the main sulphidic bulk of the matte and join the main oxidic phase forming scorifier slag. Overall, this would be a first known archaeological indication for the further refining of matte cakes – in addition to the usual scorification of bullion products – by scorification, to recover and determine the amount of precious metals that were retained in these sulphidic phases during the crucible fusion, and/or to study this type of material more closely. The generally combined high lead and iron contents of the scorifier slag layers further suggest that in some cases either matte was scorified on its own with some additional lead, or that the two materials, bullion and matte, were scorified together.

A few matte inclusions and metallic prills were found in these slag residues. When in relatively significant amount, the former corroborate the hypothesis that not only lead bullions were scorified, but that matte may have been further processed in scorifiers, separately or together with bullions. The recurrence of antimony, arsenic, copper, silver and the occurrence of gold further show that scorification was performed to further refine materials to determine their content in noble metals, and that it was almost certainly following the initial step of reducing fusion in a triangular crucible. Some scorifier slag with high levels of these various elements may, however, be the result of the scorification of very clean pieces of ores, devoid of gangue, e.g. some pure fahlores. As described in chapter 4, Agricola and Ercker both recommend the scorification-cupellation as well for gold ores, with Ercker indeed preferring this latter assaying method (Sisco and Smith 1951: 114).

The scarcity of metallic and matte inclusions in most of the slag samples – with three particular specimens showing no inclusions at all (OB 269/S1, OB 274/S1, OB 277/S1) – could imply that some bullions were clean while others were contaminated with matte, or maybe that, in some cases, bullion was scorified on its own and, in others, together with a matte cake. Another explanation for the absence of matte inclusions in these scorifier slag samples may otherwise be that scorification was not performed in one step only, but several times prior to cupellation. Making bone-ash cupels was time-consuming, and it would appear more convenient and economically more profitable to thoroughly refine the bullion or the matte by intermediate scorifications and discard the ceramic plates, before cupellation. Besides, the low amount of silica in the lead silicates (8 to 21 wt% SiO_2, average of *ca.* 14 wt% SiO_2; Table 5.7, p. 165) is typical of a melt, which did not reach its equilibrium with the silica-rich ceramic (Fig. 5.52). This may indicate that scorification was carried out rather swiftly.

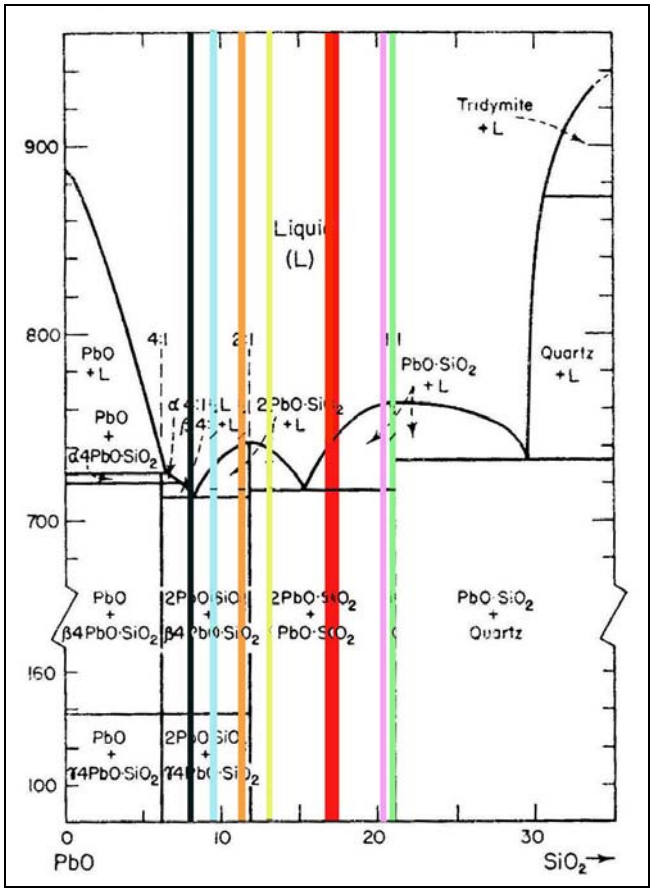


Fig. 5.52. *PbO-SiO_2 phase equilibrium diagram. The coloured lines plot the concentrations of lead oxide in the slag of, from left to right, scorifier slag OB 269/S1, OB 270/S1, OB 274/S1, OB N006/S1, OB 268/S1, OB 276/S1, OB 277/S1, OB 282/S1 and OB 273/S1. Note that for high temperatures (above 750 °C), lead would still react with any available silica (modified after Allibert* et al*. 1995: 116).*

The presence of the lead bullion layer identified in scorifier OB 282 confirms the formation of a scorifier lead bullion, which would have been taken out of the scorifier and further refined through additional scorifications and then cupellation. Its high bulk silver concentration (6 wt% Ag) further stresses the importance of noble metals in the metallurgical activities carried out in the laboratory of Oberstockstall, inferring they were the final intended products.

The resulting lead-, silver-, and gold-containing products from this scorification step would then have been taken out, to be either refined by further scorification or cupelled if considered to be clean and small enough.

5.4.2.2. Peculiar cases indicative of further experimental activities

- **Scorification: the first step of a metallurgical sequence**

Scorifier OB 281 shows two different slag layers: the first, i.e. the one in direct contact with the ceramic, having a silica- and lead-rich glassy matrix and a composition similar to the crucible slag remains characterised earlier; the second, i.e.

on top of the first, showing a lead silicate glass with fewer minor oxides than the previous one.

As with the crucible slag residues, the glass of the first scorifier slag layer (OB 282/S1 slag 1, Table 5.8) is enriched in iron oxide (10 wt% FeO), soda (7 wt% Na_2O), calcium oxide (3 wt% CaO) and potash (1 wt% K_2O), elements having a mineral or fluxing salt origin and probably suggesting that the material scorified here was an ore. Some arsenic (2 wt% As_2O_3), antimony (6 wt% Sb_2O_3) and copper (1 wt% Cu) have also been detected in that same slag (Table 5.8), showing that the scorified ore was rich in these metals. The identification of a fahlore or complex sulphidic ore, similar to the one processed in the triangular crucibles, as the raw material for this scorification step links this sample to the main set of scorifiers of the assemblage. The metallurgical sequence however appears to be slightly different in the present situation, as it seems to start directly by scorifying the ore, probably with some fluxes, without treating it in a triangular crucible beforehand. Fluxes such as the ones used in the triangular crucibles – i.e. iron filings, glass and salt (average of *ca.* 0.7 wt% Cl in glass matrix of slag) – could have been used here, producing a slag enrichment such as the one seen here. Various crystals of magnetite contain high quantities of zinc oxide (3 to 7 wt% ZnO), substantiating the mineral origin of the raw material, since zinc would not normally be part of a bullion cake. Although no sulphur has been detected in the bulk and in the glass of this slag, numerous feldspathoids with a composition similar to lazurite show up to 5 wt% of this element, which preferentially goes into these separate phases rather than in the glass and probably initially comes from the ore. Many discrete antimony oxide-rich phases (36 wt% to 52 wt% Sb_2O_3) also contain a high level of tin oxide (6 to 10 wt% SnO_2) (Fig. 5.53). This is in contrast with the other scorifier slag samples, and indicates that, although this ore was probably similar to the main group of tested minerals, its composition and probably its appearance may have differed in some way. This may have been a reason to experiment with a new procedure, as seemed to be the case with the use of antimony metal as metal collector in a triangular crucible. The high amount of arsenic would most likely be another constituent of the ore.

	Na_2O wt%	MgO wt%	Al_2O_3 wt%	SiO_2 wt%	K_2O wt%	P_2O_5 wt%	CaO wt%	TiO_2 wt%	FeO wt%	CuO wt%	As_2O_3 wt%	Sb_2O_3 wt%	PbO wt%
OB 281/S1 slag 1	7.2	0.6	6.7	34.2	1.3	b.d.l.	2.6	b.d.l.	10.4	0.7	1.6	5.8	28.3
OB 281/S1 slag 2	b.d.l.	b.d.l.	3.2	11.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.	4.9	2.2	0.4	6.1	72.3
Average of ceramic matrices*	0.4	0.6	30.5	59.7	2.7	0.3	0.9	0.7	4.0	b.d.l.	b.d.l.	b.d.l.	b.d.l.

***** after Martinón-Torres and Rehren 2005b

Table 5.8. *Average chemical composition by SEM-EDS, normalised to 100 wt%, of the glass matrices of the two slag layers within scorifier OB 281. See appendix 3 p.326 for the full results.*

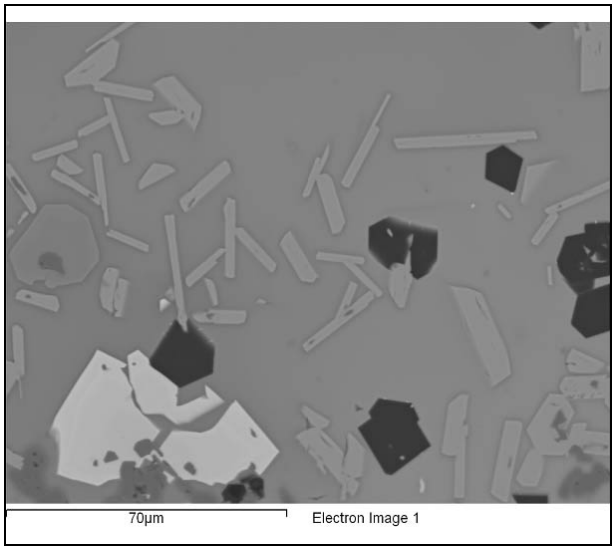


Fig. 5.53. *Magnetite crystals (pale grey), with antimony oxide-, calcium oxide- and tin oxide-rich crystals (bright) and feldspathoids (dark) in a silica- and lead oxide-rich glassy matrix (OB 281/S1, BSE, 800x).*

The second slag layer within this scorifier (OB 282/S1 slag 2, Table 5.8) has the typical composition and structure of a scorifier slag in Oberstockstall; its main matrix is a lead silicate glass (72 wt% PbO, 11 wt% SiO_2). Numerous small inclusions of copper and silver (97 wt% Cu, 3 wt% Ag) can be seen in this lead-rich glass, suggesting once again that the ore processed in scorifier OB 281 was tested for its content in silver (Fig. 5.54).

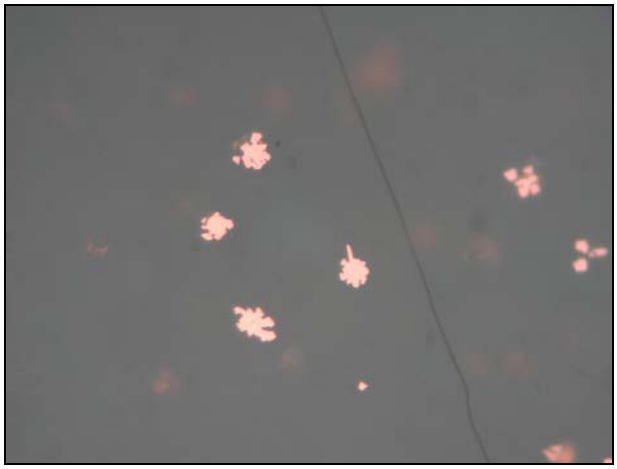


Fig. 5.54. *Bright orange silver-rich copper prills in a lead silicate glass (OB 281/S1, optical microscope, plane polarised light, 1000x, long axis ~150 µm).*

It seems here that the chymist working in Oberstockstall had decided to carry out his ore testing by using the alternative route given by Agricola (Hoover and Hoover 1950: 239) and Ercker (Sisco and Smith 1951: 39-40, 114), which is the scorification-cupellation sequence (cf. chapter 4). In Oberstockstall, the practice seems to therefore have been to melt an ore in a scorifier with lead as metal collector and iron filings, glass and common salt as fluxes. The lead bullion produced from this ore scorification would then be further scorified and finally cupelled. It can be noticed, however, that this substitute procedure seems to be less efficient that the main sequence of crucible fusion followed by scorification, due to the relatively higher silver losses trapped in copper prills identified in the slag.

- **The use of antimony as a noble metal collector**

Similarly to the slag of crucible OB 479, the slag residues within scorifiers OB 271 and OB 284 are mainly composed of an antimony oxide-rich matrix (Table 5.9). These slag remains would result from the scorification of an antimony-dominated bullion, suggesting the intended use of antimony as a collector for the noble metals during the crucible fusion. A possible picture here could be the processing of a sulphidic ore with antimony rather than lead, starting with the reducing fusion in a triangular crucible, such as OB 479, and followed by the scorification of the resulting antimony-rich bullion, and maybe of the matte as well. In fact, the antimony-rich matte cake identified in the assemblage from Oberstockstall, although interpreted as the result of the processing of an antimony-rich ore, could have been produced by such a crucible fusion using antimony metal instead of lead to collect the precious metals, this antimony initially introduced as stibnite in the charge.

Altogether, this specific situation is indicative of the fact that antimony was recognised as a different material, and treated differently, although with a very similar function to lead probably due to their similar appearances.

	Al_2O_3 wt%	SiO_2 wt%	CaO wt%	FeO wt%	As_2O_3 wt%	Sb_2O_3 wt%	PbO wt%
OB 271/S1	1.0	2.9	b.d.l.	b.d.l.	b.d.l.	92.0	4.1
OB 284/S1	2.0	6.4	1.3	5.3	1.4	65.6	18.1

Table 5.9. *Average chemical composition by SEM-EDS, normalised to 100 wt%, of the matrices of the slag samples within OB 271 and 284. See appendix 3 for the full results.*

5.4.3. Summary on the scorifiers

Most of the slag samples from the scorifiers have shown similar chemical compositions. Their main matrix is a lead silicate with variable amounts of silica and other oxides in relatively low concentrations. The high lead oxide content informs about the scorification of a lead bullion probably produced in a triangular crucible, which would be subjected to this oxidising reaction in order to remove more of the base metal oxides into the lead-silicate slag and simultaneously reduce the size of the bullion itself prior to cupellation. Scorification of matte seems to have also occasionally taken place, most likely to assess the amount of silver lost in this phase, and for this, some silver-free lead may have been added to ensure the extraction of the precious metals from the matte and their collection by the molten lead metal phase. Joint scorification of lead bullion and matte is another possibility for potential reasons discussed later (cf. chapter 7). Scorifying the matte, on its own or together with the bullion, would result in a more accurate quantitative assessment of the amount of precious metals primarily contained in the ore. In any case, the bullion generated by the first scorification would be further scorified, possibly several times, to reduce its size before being cupelled.

Several scorifier slag remains include oxidised prills of antimony, lead and copper, while two have sulphidic inclusions. These different residues have also most likely been created by the scorification of lead bullion, sometimes still contaminated by crucible slag or matte inclusions, or possibly by the scorification of matte, leaving behind separate sulphidic phases and/or small globules of metal in the slag. Silver

has been identified in metallic prills of various samples, once again pointing to the likely test of ores for their content in silver.

It has furthermore been identified that, in one particular case, scorification was the first step of the metallurgical sequence, which is one possible route to process ore according to the sixteenth-century books (cf. chapter 4). Another variation of the typical reaction scheme seems to have been the use of antimony as noble metal collector, which has been documented for the crucible fusion and appears to be further indicated by the scorification of an antimony bullion. These variations to the main sequence of operations once again emphasise the research aspect of this laboratory.

Once the lead bullion had reached the desired size and concentration, it would have finally been cupelled.

5.5. Cupellation: the final high-temperature step of the fire assay sequence

This section only briefly reports the previous scientific studies carried out on the cupels from Oberstockstall, as their analysis has already been detailed and published elsewhere. These analyses initially indicated that the cupels were made of a mixture of bone ash and clay (Rehren 1998), but the data were recently re-interpreted and more specimens analysed to clearly show that these cupels were instead composed of a mixture of bone and wood ash (Martinón-Torres *et al.* 2009). The bodies of used cupels are soaked with lead oxide, now mostly transformed into secondary carbonates which filled the pores of the original structure (Fig. 5.55). Varying amounts of metals, such as gold (20-100 ppm Au), silver (100-500 ppm Ag), copper (0.03-2.80 wt% Cu), antimony (500-2500 ppm Sb), bismuth (700-2500 ppm Bi with two cupels showing 12.2 and 25.2 wt% Bi), arsenic (200-1000 ppm As), and zinc (50-300 ppm Zn), have also been detected by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), relating these to the previous metallurgical residues (Rehren 1998: 345; Martinón-Torres and Rehren 2005b). The presence of impurities such as copper, antimony, arsenic, bismuth, and zinc further support the interpretation presented above, that the raw material processed through the technical sequence identified in Oberstockstall was a mineral, and these elements fit well with the fire assaying of a fahlore for its content in precious metals.

It is worth highlighting the high amount of bismuth detected in two of the cupels, as these appear to mirror the crucible matte remains displaying locally high

concentrations of this element, generally associated with antimony. Bismuth, in a similar way to antimony, was not properly known as a metal in its own right, nor its properties understood. Its presence among the metallurgical remains in such high quantities may indicate experimentations performed on this element and reflect the overall context of the laboratory Oberstockstall and the mindset of its chymists, well inclined towards researching new materials and therefore not always following standardised procedures.

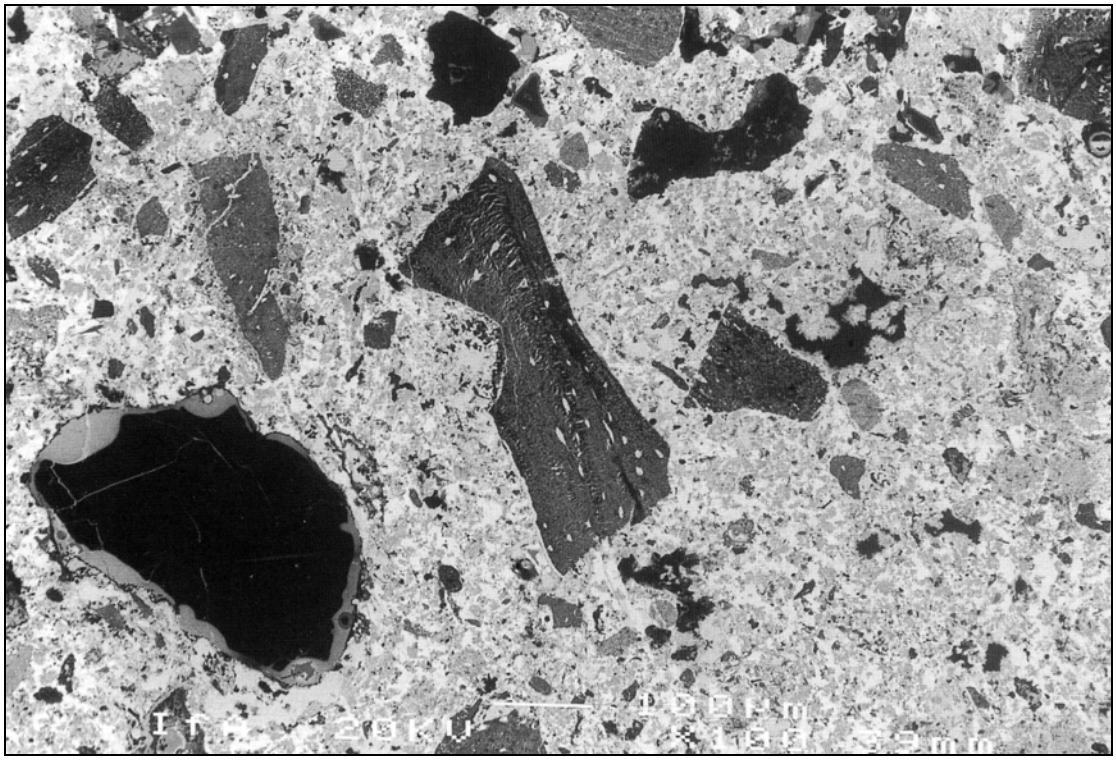


Fig. 5.55. *BSE image of the microstructure of a used cupel from Oberstockstall. Note the dark crystal of quartz (bottom left) and the bone apatite particles (large on in the centre of the picture) in a bright matrix of lead oxide, now mostly weathered to lead carbonate (after Rehren 1998: 341).*

Cupellation would thus constitute the last high-temperature operation, necessary to obtain a clean button of noble metals, completely free of lead. If both gold and silver where alloyed in this final product, they could be parted using mineral acids, which would explain the presence of distillation equipment and glass ware in the assemblage.

The analytical results of the cupels seem to match other studies on the same type of material and related to minerals from the same period or slightly earlier (Thomas *et al.* 2006; Martinón-Torres *et al.* 2008; Martinón-Torres *et al. in press*). Their

study was included here as this step concludes the high-temperature *chaîne opératoire* to which sulphidic ores were submitted in order to extract their contents in noble metals and because this operation allows to finally produce the expected bead of precious metals.

5.6. Summary of the archaeometric study of the material from Oberstockstall

The study of this unique assemblage is the key to the understanding of chemical and metallurgical sixteenth-century laboratory practice. From the analysis of the various metallurgical residues, the main high-temperature sequence identified in Oberstockstall consisted of three steps, namely crucible fusion, scorification and cupellation, with ores containing precious metals as raw materials. The initial step involved the fusion of the ore in a triangular crucible, with lead as metal collector for the precious metals, and iron filings, crushed glass and/or salt as fluxes. The products of this opening stage included lead-rich bullion, matte and slag. The former, lead bullion, was scorified while the latter, slag, was discarded. It seems that the lead bullion to be scorified was often contaminated by crucible matte, either as small fragments attached to it or as inclusions within the metallic phase; and probably by some slag as well. In some cases, it is also possible that matte, which has been found in this archaeological assemblage and therefore appears to have been kept for specific purposes, was also scorified in order to recover and/or assess its content in precious metals or for more general research studies on its properties. The resulting lead bullion was probably scorified more than once to be reduced in size and to remove as much impurities as possible. The bullion produced by the final scorification, and which hopefully contained all the precious metals originally part of the ore, was finally cupelled to form a gold-bearing silver button (Fig. 5.56).

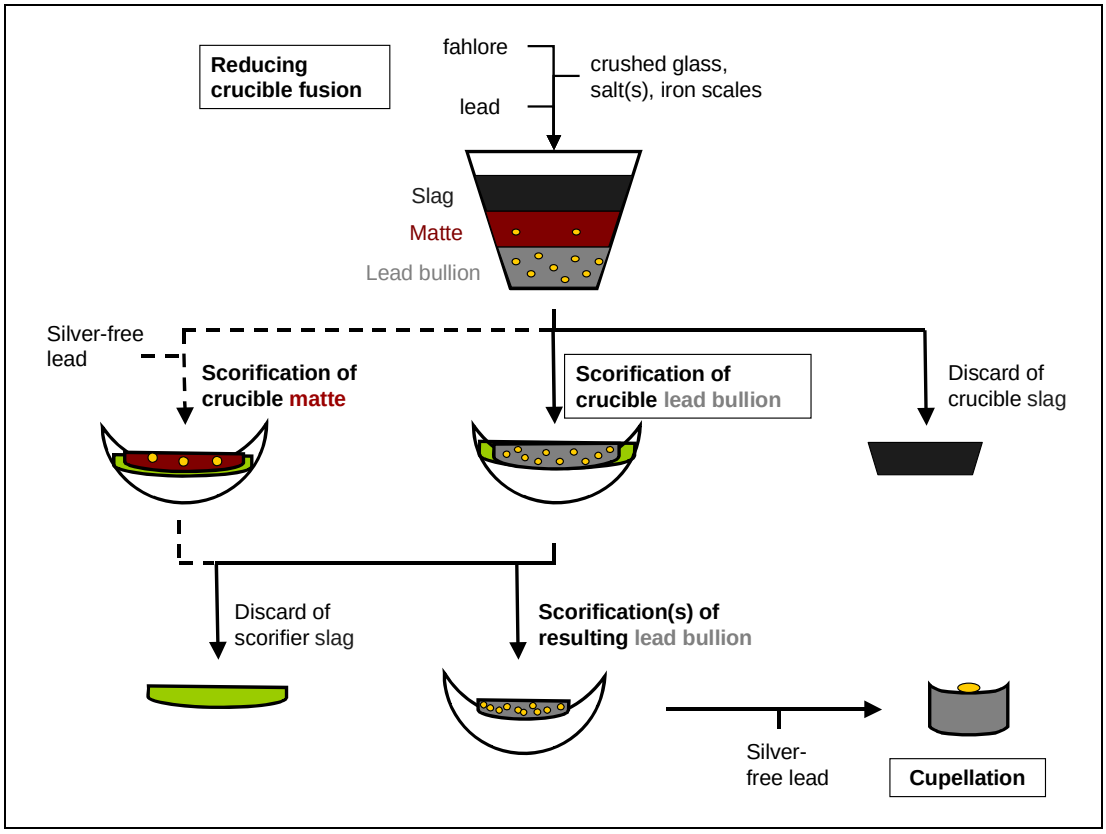


Fig. 5.56. *Diagram presenting the main technical sequence identified in Oberstockstall through the analysis of the residues of the various high-temperature stages.*

The gold-silver alloy could have been additionally refined by separating the two precious metals. Potential methods for this include cementation with salt and parting with sulphur, antimony sulphide, or mineral acids. Several chemical apparatus and technical glassware, such as flasks, phials, cucurbits, retorts, and alembics, were excavated from the laboratory of Oberstockstall (Von Osten 1998: 80-81, 112, 200-208), and could be interpreted as having been used in parting, distillation – such as the distillation of parting acid – or cementation (Bayley 2008) (Fig. 5.1, p. 111, and 5.57). The reconstruction of a potential distillation furnace is displayed in the *Museum der Alchemist* in Oberstockstall (Fig. 5.58); the way it has been recreated from however small archaeological evidence closely matches the contemporary representation of such furnaces as given for instance by Libavius (Fig. 5.59). Overall, the type of equipment found in the laboratory of Obersockstall strengthens the probability of acid parting being carried out, rather than cementation, together with practice of a very wide range of chemical activities.

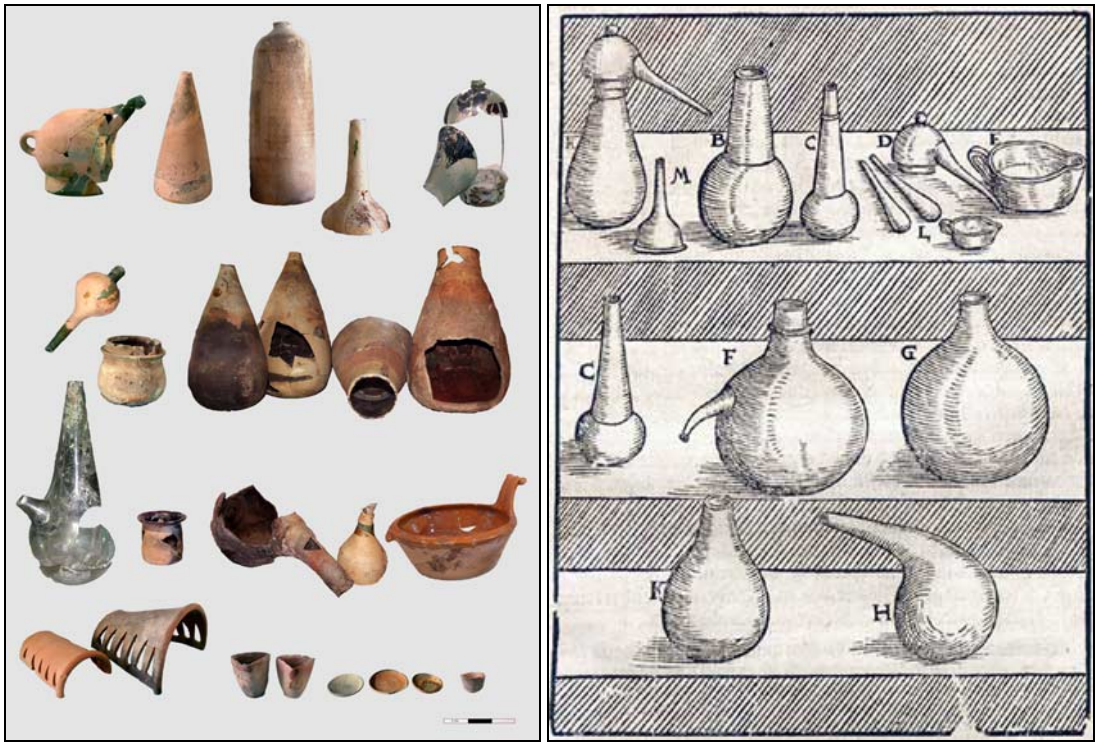


Fig. 5.57. *Technical ceramic and glass apparatus from Oberstockstall (left; scale bar 15 cm; photo: M. Martinón-Torres), interpreted as being used in the processing of ores for their content in precious metals. Note the alembic (top left) and the glass distillation flask (third row, left), among other flasks, phials and funnels. Triangular crucibles, scorifiers, cupels, and muffles, which were used in the high-temperature reactions of the metallurgical sequence, are shown at the bottom. Notice the similarities between the various archaeological reaction vessels with their contemporary depiction by Ercker (right, after Sisco and Smith 1951: 142).*

Fig. 5.58. *Reconstruction of a distillation furnace from excavated brick fragments, vessels and plugs, Museum der Alchemist, Kirchberg am Wagram, Austria (photo: M. Martinón-Torres).*

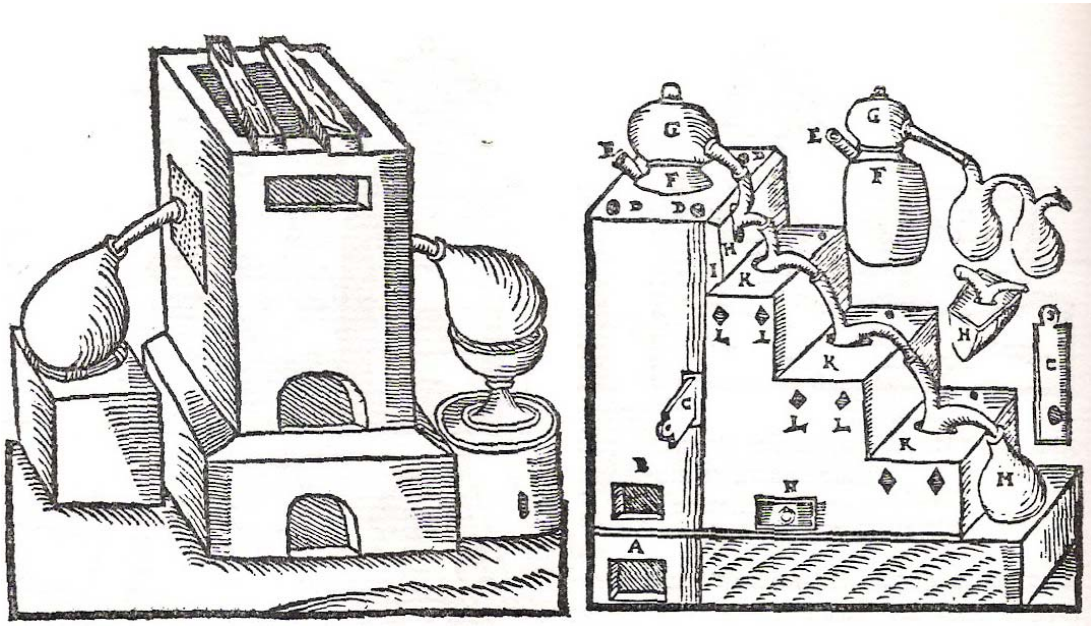


Fig. 5.59. *Distillation furnaces depicted by Libavius: note the double retorts (left), and the multiple holes for the plugs (marked L) (right) (after Atterer* et al. *1964: Bildteil 66-67).*

In addition to this primary procedure, there are several distinct metallurgical operations, which appear to be part of a wide set of practical experimentations. One of these tests seems to be the substitution of lead by antimony as metal collector, as suggested by the very antimony-rich residues within one triangular crucible and two scorifiers. Another is the enigmatic dominance of bismuth among two cupels (Rehren 1998), which is matched by no other residue analysed, but one single matte cake. There could be various implications and interpretations to this particular sequence, since antimony and bismuth were arguably not metals known as such at that time, but seen as 'variants' or 'species' of lead (Hoover and Hoover 1950: footnotes 110, 428-429, 433). One reason for trying these unusual 'metals' may have been due to their similar appearance and physical properties to lead metal, and the consequent belief that they would probably chemically react or behave in a similar way to that more common and soft metal. Actual research may be an alternative explanation: it could have been a laboratory in the modern meaning of the term. In that context, it would seem logical to see variations to the main set of reactions, which would allow for the study of new elements and materials and the attempt to understand their physical and chemical properties. This research aspect seems to be further stressed by the high amounts of bismuth detected in several samples from crucibles, matte and cupels, suggesting that similarly to antimony, this metalloid may have generated a real interest to the Oberstockstall chymists, who may have wanted to experiment – "play" in a way – with it.

A modified version of the primary procedure also appears to have been performed; this is the direct scorification of the ore as the first step of the sequence – i.e. without the reducing crucible fusion – with possibly the same fluxes as used in the triangular crucibles. As mentioned before, the ore processed through this specifically distinct route appears to have been different, probably richer in arsenic and tin than the main fahlore. This variation in the method used seems to further indicate the "Research and Development" character of this laboratory: it appears that the metallurgical sequence has been potentially adapted to satisfy different requirements. Thus, besides the attempt to use and understand unknown materials, it would appear that the experimentation of new reaction schemes were conducted, depending on initial parameters, such as the nature of the raw material.

Although one main metallurgical process seems to have been routinely followed, there are clear disparities existing between several methods, which seem to have been motivated by different reasons. The identification of these alternative routes, either initiated by the processing of different raw materials or the use of unknown materials as additives, leads to the discussion of the level of awareness of the individuals using this laboratory and the purpose of their metallurgical and chemical activities. These broader matters will be fully explored in a later chapter, by comparing these data to relevant studies and to contemporary written sources (cf. chapter 7). Beforehand, the next chapter will present the results of the scientific study of the remains from a sixteenth-century smelting site, which will also be used as a comparison to the Oberstockstall laboratory, in this later chapter, in order to investigate the full range of metallurgical activities associated to precious metals in early modern Europe.

Chapter 6 – Gold smelting in Renaissance Central Europe: the metallurgical remains from the Angertal

6.1. Overview

The excavation of the gold smelting site of the Angertal, located in the region of Gastein, uncovered large quantities of material, which required carefully thought-out sampling, as previously explained (cf. chapter 3). The Angertal was a significant region of production of noble metals in the sixteenth century, and almost no archaeometric study of the early modern industry of noble metals in the Old World currently exists. There are references in written sources to metallurgical activities in this area of Central Europe through the Middle Ages and the early modern period and to their link to gold mines located in the surrounding mountains, such as the Bockhart and the Erzwies. Besides, the excavated features of the site itself, such as furnaces and slag heaps, were typical of a large-scale smelting site (Cech and Walach 1999; Cech and Walach 2001). Thus, the assemblage offered a unique opportunity for further study to identify the metallurgical processes and reactions carried out at this site in order to develop our knowledge of high-temperature technologies applied in the primary metallurgy of noble metals in early modern Europe. This case study was also very relevant to the overall research topic of this project since it is contemporary to the complex laboratory of Oberstockstall and presents similarities with this site, although the scale and context are significantly different. This allows a further opportunity to compare archaeological reconstruction to textual information and to approach the potential 'intentionality' behind the materials. For the purpose of this analytical study, a variety of materials from the excavated plant – site H1 presented in chapter 2 (Fig. 6.1.), that is also the best of the eight known smelting sites in the Angertal – has been selected, from numerous slag fragments of various kinds, pieces of ore and other waste products from smelting operations, to furnace wall fragments, and less typical but potentially relevant samples. A relatively large number of pieces of ore from the close contemporary mining sites of the Bockhart and the Erzwies have also been characterised, in order

to compare their compositions with those of the waste products, since these minerals were potential raw materials for smelting in the Angertal.

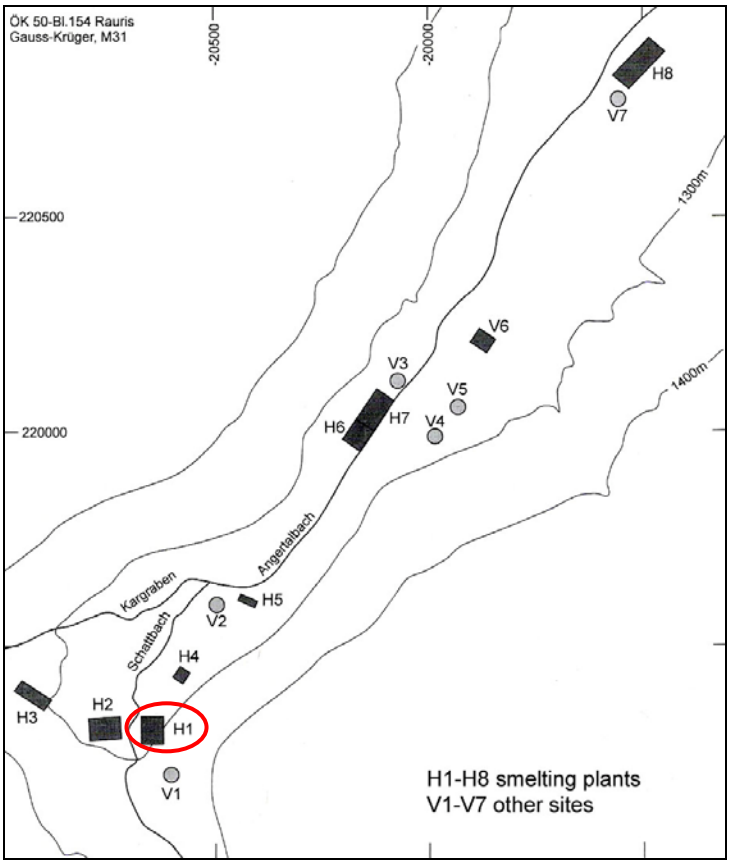


Fig. 6.1. *Map of the smelting sites located in the Angertal. The material studied here comes from the excavated smelting plant H1 (modified after Cech and Walach 1999: 481).*

This chapter presents the selected archaeological material from the excavated mining site of the Bockhart and smelting site of the Angertal, as well as surface ore samples from the survey of the mining area of the nearby Erzwies. The chemical study of the ores from both mining areas indicated that they were very similar and it has therefore not been possible from the analytical data to precisely ascribe an origin to the ores smelted in the Angertal, since both areas, and potentially others in the surrounding mountains, present very comparable mineral formations. Historical sources, however, report that the Angertal site was indeed supplied by these two mining disctricts between the late medieval and early modern periods (Cech and Walach 1999; Gruber 2000; Cech and Walach 2001; Cech 2007, C. Bartels, *pers. comm.*). The analytical study of the different raw materials, waste and products from smelting activities, however, allowed the reconstruction of high-temperature

processes carried out at one of the eight known smelting sites of the Angertal in the heyday of its activity in the second half of the sixteenth century. The results from these analyses combined with the archaeological data enabled an understanding of the organisation of smelting operations on an industrial scale in this part of Europe, which was central to the production of noble metals – and base metals as well – at that time, in competition with the gold and silver arriving from the New World.

This chapter begins with a brief summary of the technological reconstruction of the *chaîne opératoire* of the metallurgical process identified in the Angertal, before detailing the data, which support this reconstruction. Mixtures of sulphidic ores containing gold and silver and bearing a gangue of quartz and manganese-rich iron carbonates seem to have been smelted simultaneously in three furnaces, using charcoal as fuel and bellows for the supply of air (Cech and Walach 1999; Cech and Walach 2001). A dressing plant has been identified in the Bockhart (Cech and Walach 2001; Cech 2007: 62-78) and was probably used to beneficiate the ore before transporting it to the smelting site down in the Angertal. The mixture of beneficiated ore with a relatively consistent amount of gangue was most likely self-fluxing, and the only additions to the charge in the furnace were probably the charcoal as fuel and possibly some lead metal. The quantity of lead already present in the mixture of ores in the form of galena may have been sufficient to avoid this addition of lead metal, but the transport of lead metal for the smelting of ores containing noble metals reported in sixteenth-century historical texts (Gruber 2000: 164) may suggest otherwise. The chemical and metallurgical reaction taking place in the furnace led to the formation of a lead bullion at the bottom, which collected the noble metals, on top of which was an intermediate layer of matte, which was itself covered by an upper layer of slag. All three layers separated by density. The slag and the matte were both tapped out of the furnace. The formation of matte further indicates that sulphur was not completely removed through roasting and that the ore was most likely only partially roasted. The apparently relatively small quantity of matte compared to slag[3] suggests that matte may have been added to pieces of ores to be smelted again. The metallic lead bullion was most likely subsequently cupelled

[3] This observation has been made by the author on the overall quantity of excavated material made available from storage, which was a random sample of the whole archaeological assemblage and appears to be holding a lot more slag than matte. No quantification has, however, been done by the archaeologist during the excavation of the site, as matte had not been fully recognised at the time, and was believed to be slag (B. Cech, *pers. comm.)*.

in a cupellation hearth, such as those described by Agricola or Ercker (Fig. 6.2). Evidence of such a structure or of cupellation remains, such as litharge cakes or hearths soaked in litharge, has however not been found at the excavated smelting site of the Angertal, suggesting either that further excavation may be needed to discover a construction of that kind or that the bullion was transported elsewhere to be cupelled.

Fig. 6.2. *Reverberatory furnace used in large-scale cupellation, according to Agricola (Hoover and Hoover 1950: 474).*

A second important aspect of the study of this site relates to experimental cupellation of archaeological materials. As previously mentioned, the noble metals collected by the lead in the furnace would be separated from it by cupellation as the final high-temperature step of the *chaîne opératoire*. It has not been possible to directly characterise this cupellation here due to the absence of archaeological remains associated with this activity at the Angertal smelting site. Instead, several archaeological samples of lead and matte from the smelting operations were cupelled in modern bone-ash cupels in an electric furnace, in order to assess their content in precious metals. The silver-gold beads produced by this process were analysed by scanning electron microscopy-energy dispersive spectrometry and micro X-ray fluorescence. The relative proportion of gold and silver alloyed in the beads obtained by cupellation helped in the determination of the economic value of the ores, and indicated that the minerals processed at the Angertal smelting site were exploited for their gold content as well as for silver, as stated by Renaissance written sources

(Cech and Walach 1999; Gruber 2000; Cech 2007). After this final process, the noble metals were then most likely parted and distributed to gold- and silversmiths, mints and other gold workshops closer to urban centres. Written sources report in the sixteenth century the transport of the silver-gold alloy to Salzburg, where gold and silver were parted and each metal used in the local mint (Gruber 2000: 165). Cross-sections of the experimental cupels were also studied and analysed to identify the nature of the base metal oxides and verify if any precious metals were lost during the operation. The analyses of these cupels will also be compared to the analytical data obtained on the archaeological cupellation remains from the laboratory of Oberstockstall to establish further similarities or differences between the two case studies (cf. chapter 7).

This chapter will explain how the reconstruction of the history of this site has been drawn from the combination of an archaeological, historical and archaeometric study of excavated material. It starts with a macroscopic description of the various finds from the mining and the smelting sites, follows by the presentation of their microstructural and analytical study and concludes with the discussion of the data.

6.2. Macroscopic description of the finds

6.2.1. The mines of the Bockhart and the Erzwies

In previous geological publications on the Gastein region and archaeometric studies of ore samples from the Angertal and the Bockhart, the main minerals containing gold and silver were identified as quartz, pyrite and arsenopyrite (Hauptmann and Rehren 1990; Gstrein 1993). An arsenopyrite vein had also been identified through geomagnetic and geoelectrical prospecting of mining terraces (Cech and Walach 2001: 298; Cech 2007: 7). The present research, however, seems to show slightly different results.

It had been stated in earlier stages of this research project that arsenopyrite had not been identified as one of the main minerals. This was mainly based on the absence of arsenic oxide at significant levels in the analysed slag samples (Mongiatti *et al.* in press). The analysis of a larger set of samples, especially of additional ore specimens, has now given a clearer picture of the situation. The results of this more comprehensive microscopic study of the minerals from the mining areas seem to suggest that arsenopyrite was indeed part of a very wide variety of minerals, which

was extracted from the mines and potentially smelted in the Angertal. The actual minerals smelted in the Angertal should remain more clearly identifiable through the analytical study of the slag, the mineral assemblage recognised at the mining sites simply showing what might have been available.

All pieces of ore appear clearly weathered, covered by layers of dusty corrosion. Most of these show either a light cream or reddish-brown colour on their outside. The former is typical of lead sulphide which has corroded to lead carbonate and suggests that galena is most probably a major component of the ores, while the latter is indicative of a high amount of iron and therefore of the possible presence of pyrite and/or arsenopyrite (Fig. 6.3). Optical microscopy of cross-sections, presented later in this chapter, was however necessary to reliably distinguish between the various sulphidic ores. This was combined with ED-XRF analysis in order to determine the relative proportions of the sulphides and gangue components present within these selected minerals, and identify their content in precious metals (Table 6.1, p. 204).

In the Bockhart, the selected ore fragments have been excavated from various places of the mining site, the map displayed below indicates their different find spots (Fig. 6.4). A relatively high number of ore pieces was found outside the south-west corner of the smithy building among the stones of a collapsed wall. From the stratigraphy of the site, these may be the products of an ore prospecting episode, which took place after the abandonment of the mining site at the very beginning of the seventeenth century and when part of the building had already collapsed. These ores may not be directly relevant to the Angertal smelting process, but they are informative of the overall local geology. From their very standardised and relatively small size (Fig. 6.3), these minerals have most likely been initially sorted and possibly gone through a coarse crushing at the ore dressing plant nearby, although this dressing plant seems to have no longer been in operation after the mine was abandoned. They could be connected to the small assaying furnace found inside the smithy building. This small furnace sits on top of the iron finds, which had fallen from the shelves when the latter collapsed and were scattered on the floor of the smithy; this structure therefore most probably also belongs to a later phase of ore prospecting (Cech 2007: 51).

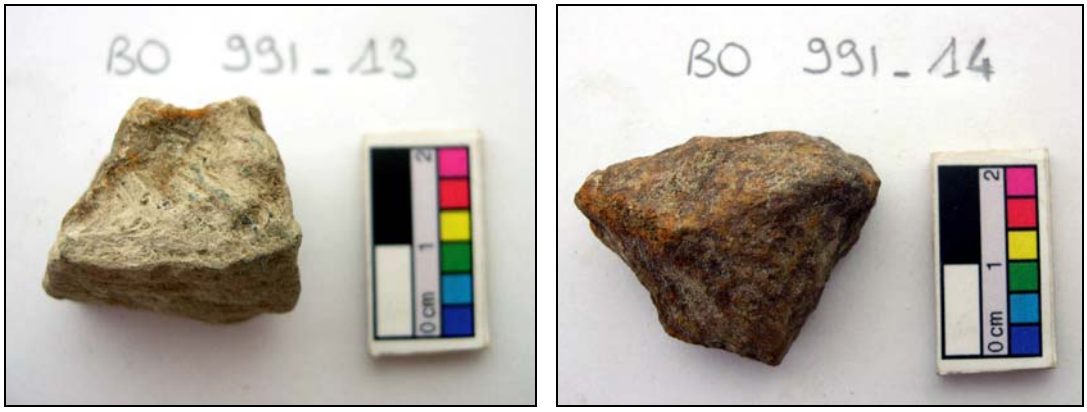


Fig. 6.3. *Mineral fragments from the Bockhart mining site found close to the smithy: weathered galena on the left and an iron-rich sulphidic ore on the right (left: BO 991-13; right: BO 991-14; scale bars 2 cm; photos A. Mongiatti).*

Pieces of ore from the Erzwies mining site have been collected from the ground level while surveying the area (B. Cech, *pers. comm.*). These fragments of sulphidic minerals could come from various levels or periods of exploitation of the mines, and their composition may not be representative of the veins exploited in the sixteenth century. Besides, the Erzwies area displays large heaps of minerals, which have been discarded after initial sorting at the mine (C. Bartels, *pers. comm.*); the pieces of ores therefore gathered may be part of the minerals considered useless by the ancient miners. It was hoped, however, that they would provide a general impression of the ore minerals present. Their appearance is very similar to that of the Bockhart ore fragments.

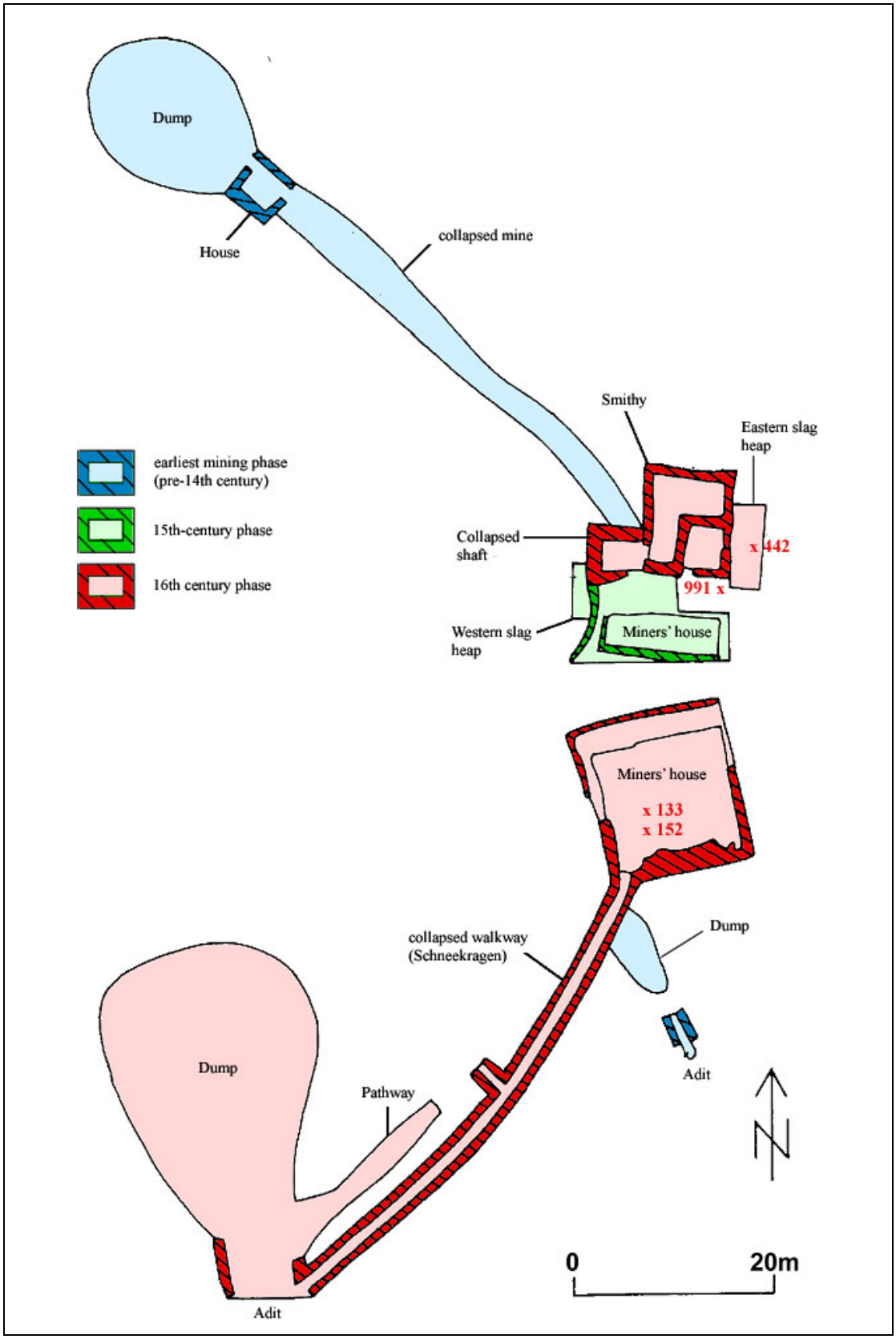


Fig. 6.4. *Map of the excavated mining site of the Bockhart indicating the find spots* ***(x)*** *of ore pieces selected for this research (modified after Cech 2000; Cech and Walach 2001; Cech 2007: 18).*

The excavated fragments of ore from the mining site of the Bockhart, as well as the surface finds from the Erzwies mining area were analysed to compare the types of ore and slag from the smelting and mining sites, and further try to understand how metallurgical operations were organised and carried out at the Angertal site.

6.2.2. The Angertal smelting site

The various samples from smelting site H1 initially selected for this project were taken from different locations and contexts of the stratigraphy within the archaeological site to allow the results of the study to be as representative as possible of the whole excavated area. A map of these chosen remains has been drawn in order to record their precise location (Fig. 6.5), in a similar way to the Bockhart one (Fig. 6.4). Most of the analysed finds come from archaeological layers at stratigraphic levels contemporary to the excavated features of the sixteenth-century smelting site. Some areas were however disturbed after this site was abandoned and buried, since several finds clearly belonging to the same site and produced by the same early modern metallurgical activity were moved into higher layers of the ground, i.e. more recent, than the level of the sixteenth-century plant itself.

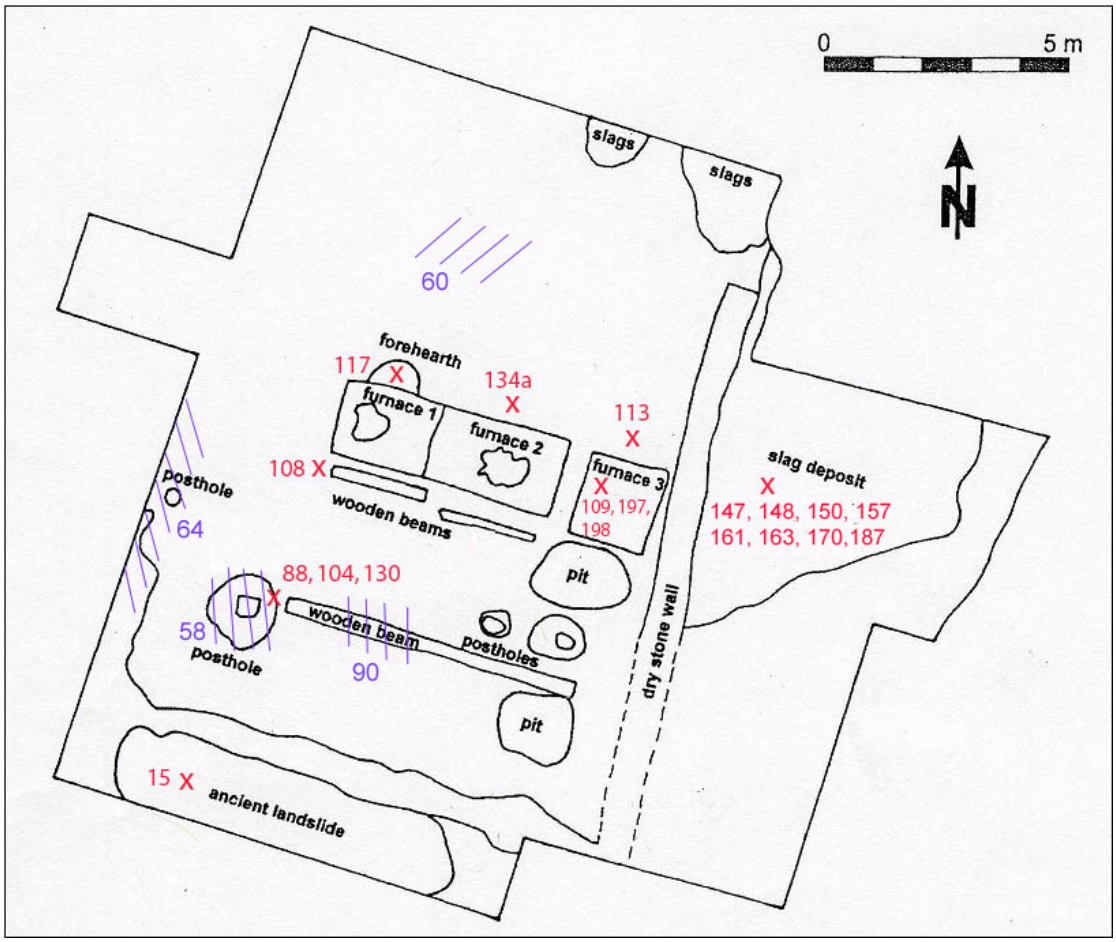


Fig. 6.5. *Map of smelting plant H1 showing the archaeological contexts of the samples selected for analysis. Stratigraphic layers shown by crosses are at the same level as the features drawn on this plan of the site, while contexts indicated by bars were situated at higher levels. The finds recovered from the latter contexts have probably been moved from their original location but most likely came from the smelting plant (modified after Cech and Walach 2001: 310).*

6.2.2.1. Slag fragments

The slag fragments collected from the site macroscopically show a wide range of variation in shape, size, colour, texture, porosity and degree of corrosion (Fig. 6.6-6.7). Most of these pieces of slag are black, platy, more or less porous and/or rusty, with different surface textures. Several others, occurring in relatively smaller amounts are bulky, grey, with rusty or green areas of corrosion products. The rust-coloured areas and/or corrosion products suggest that they probably contain a relatively high amount of iron. The typical thinness and platy shape of the majority of the slag samples seems to indicate that the slag was tapped out of the furnace, possibly in a forehearth, and left to cool there, rather than being left to solidify in the furnace and having the latter broken open to recover the metal at the bottom. The

hypothesis of the slag being tapped is further stressed by the discovery of pieces of 'channel slag' among the finds; these are fragments having the characteristic shape of a channel through which the liquid slag was probably running when coming out of the furnace. When the slag later solidified on cooling, it kept this diagnostic shape (Fig. 6.8). Besides, peculiar textures of what appears to be the top surface of several pieces of slag show a texture characteristic of flow and the probable use of a hooked bar to remove the skin of solidifying slag forming on top of the matte and bullion in the forehearth after tapping (Fig. 6.6 left and 6.9).

Fig. 6.6. *Two macroscopically different groups of slag: the main type of slag being black and platy with a surface texture characteristic of a liquid (AN 113, left); a relatively less significant quantity of bulky and rusty slag (AN 90, right) (scale bars 5 cm; photos: A. Mongiatti).*

Fig. 6.7. *Sample of a very porous and rusty black 'platy' slag (AN 130, scale bar 2 cm; photo: A. Mongiatti).*

Fig. 6.8. *Upside down section view (left, scale bar 2 cm) and top view (right, scale bar 5 cm) of a typical 'channel slag' (AN 60; photos: A. Mongiatti).*

Fig. 6.9. *Typical surface texture of a black platy slag, suggesting the use of a rod during slag tapping (AN 147, scale bar 5 cm; photo: A. Mongiatti).*

6.2.2.2. Matte layer

Another typical waste product found at this site is matte: a fairly high number of matte fragments has been found, although in much smaller quantities than platy slag. All these pieces of matte are thin and platy, with a black and relatively porous core; they are covered with green and rusty corrosion products, probably indicative of the presence of copper and iron in their bulk (Fig. 6.10-6.11). Similarly to the crucible matte recovered from Oberstockstall and to the slag described above, the matte formed in the furnace took on a shape characteristic of the way it has cooled.

Similarly to the three layers forming in the triangular crucibles of Oberstockstall, matte would form because of the presence of non-oxidised sulphur-containing raw materials and/or reagents in the melt, in between a very dense lead-rich bullion and a lighter slag layer. Agricola mentions this situation of obtaining three distinct phases

(Hoover and Hoover 1950: 381), while Ercker suggests to initially smelt pyritic gold concentrates from amalgamation into 'slag-matte'; a same process would be applied to non-pyritic gold concentrates but with additional pyrites (Sisco and Smith 1951: 105). Like the upper layer of slag, this intermediate matte layer was probably tapped out of the furnace, as indicated by its platy shape. As seen in chapter 4, Agricola clearly describes the tapping of 'cakes of melted pyrites' (Hoover and Hoover 1950: 381), which undoubtedly correspond to matte layers being taken out of the furnace into a forehearth. A similar procedure can be found in Biringguccio's text, where he explains that the materials tapped consist of three different layers, clearly identified as bullion, matte and slag (Smith and Gnudi 1990: 154).

Fig. 6.10. *Platy matte fragments from the Angertal site from two distinct contexts, one being close to the posthole at the back of the ventilation system (AN 104, left, scale bar 10 cm) and the other close to furnace 1 and the wooden beams at the front of this same bellows installation (Fig. 6.5) (AN 108, right, scale bar 5 cm; photos: A. Mongiatti).*

Fig. 6.11. *Very rusty piece of matte, slightly different in appearance to matte samples from archaeological contexts AN 104 and AN 108 (AN 147, scale bar 5 cm; photos: A. Mongiatti).*

6.2.2.3. Furnace material

A few fragments of furnace walls have been found at this site close to the location of the furnaces and in the slag heaps. Similarly to the sample shown below (Fig. 6.12), most of these ceramic pieces show clear vitrification on one side, resulting from their exposure to high temperature. Several samples of non-vitrified refractory ceramic were selected for analysis in order to identify the type of clay mixture used and the potential occurrence of a lining on the inner surface of the furnace wall applied for additional protection of the ceramic material, as recommended by Renaissance authors (Hoover and Hoover 1950: 376-378; Smith and Gnudi 1990: 149).

Fig. 6.12. *Top (left) and section (right) views of a fragment of vitrified furnace wall (AN 163, scale bars: 10 cm (left) and 5 cm (right); photos: A. Mongiatti).*

6.2.2.4. A significant find: the bottom remain of a furnace

A very large and heavy piece (AN N01) was discovered still attached to the bottom of furnace number 3, the furnace at the eastern end of the series of furnaces (Fig. 6.5). A macro cross-section of this find showed this to be mostly a stone slab with different layered residues (Fig. 6.13). A detailed view of the left side of this fragment more distinctly revealed the various layers of which it is composed (Fig. 6.14). Metallic lead can clearly be seen in various areas of the find, as a very thin line at the bottom and as a thicker layer attached to the stone in a hole. Small pieces of platy slag can also be noticed at the far left of the fragment; another chunk of slag and most probably matte showing two different shades of grey can be seen on top of

the hole above the lead metal. The various materials of this heterogeneous and composite find have been studied and analysed in detail.

This find is of particular relevance in the discussion of issues such as the organisation of the site. There are a few possibilities in the way the three furnaces were operated: they could either be run in parallel with the same batch recipe for any kind of ores or mixtures of ore, still simultaneously run but assigned to specific ores or ore mixtures, which despite identical processes could then lead to slight variations in the charge and/or added fluxes in each furnace, or finally in series, i.e. one after the other, for consecutive processes. The last method would mean that after the initial smelt in the first furnace, matte and other suspected valuable waste products were processed further in a second furnace with different fluxes, and again further in the third furnace. The composition of the slag, matte and metal of the find from furnace 3, if different from the other furnaces, would indicate that the furnaces were run in series; in the case of similar materials being found at all three furnaces, it may on the contrary suggest that they were working concurrently. Representations of smelting operations by Agricola actually show three furnaces running at the same time (Fig. 6.52, p. 239).

Fig. 6.13. *Sliced fragment of the large oval piece found at the bottom of furnace number 3. Note the very thin layer of lead at the bottom (1a) and the one in the middle under the long hole (1b); the very heterogeneous dark grey and white streaked rock (2) and the more homogeneous 'double' grey slag and matte, middle left (3), covered by a thick layer of reddish-brown corrosion products mixed with elements from the surrounding burial environment at the top (4) (AN N01, scale bar 15 cm; photo: A. Mongiatti).*

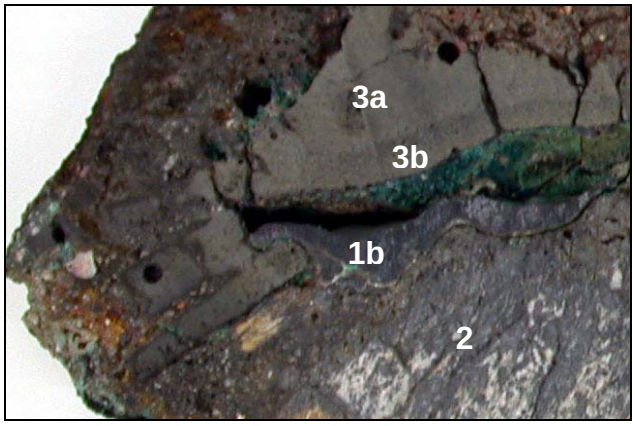


Fig. 6.14. *Detail of figure 6.13 showing platy slag (3a) and matte (3b) layers of different thickness (left and top), and metallic lead (1b) stuck to the rock (2) in the pore (AN N01).*

6.2.2.5. Ore samples

A few ore samples, which appear from their aspect and analysis to be similar to minerals from the mining sites, have also been recovered from the Angertal, scattered across the site in various levels of the stratigraphy (Fig. 6.15).

It was hoped that the analysis of ore samples from the smelting site would allow comparing their chemical composition with that of the minerals from the mining sites, in an attempt to correlate the analytical data to the historical sources, which mention the Erzwies and the Bockhart as suppliers of the smelting plants of the Angertal (Gruber 2000; Cech 2007, C. Bartels *pers. comm.*). Besides, for the latter, tracks from the transportation of the ores from the mine to the smelting centre by sliding bags called "Sackzug" down the slope of the mountain, are still visible today (Cech 2007: 177). This known relationship between these mines and the Angertal did, however, prove difficult to establish using only the archaeological and scientific data, since the ores from both mining sites were of a similar nature, which could be expected for such a region rich in complex mixtures of sulphidic ores. A second problem may come from the ore samples from the Angertal possibly being too dissimilar, if they date to later periods exploiting deeper parts of the deposits.

The composition of analysed pieces of ores from both mining sites – and from the Angertal (see below) – was also contrasted with that of the slag, in order to help in the identification of potential fluxes during the smelting process.

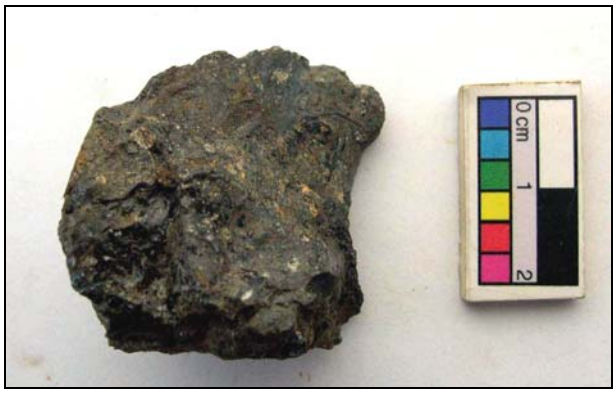


Fig. 6.15 . *Ore sample from the Angertal smelting site H1 (AN 90; scale bar 2 cm). Note that this sample has been found in more recent layers (Fig. 6.5) (photo: A. Mongiatti).*

Several sixteenth-century sources clearly state that large-scale primary metallurgy was taking place in the Angertal, which seems to be confirmed by the diagnostic excavated material studied macroscopically. There are, however, no written accounts of the methods employed by the smelters at these specific plants or known archaeological evidence of medieval and early modern smelting techniques for gold-rich ores. A thorough microscopic investigation of the various finds was therefore necessary to address these technical issues, and to further attempt to understand the reasons and incentives behind the possible technological choice of specific procedures.

Slag and ore fragments suspected to be most relevant to this detailed scientific study were selected and further submitted to microstructural and compositional analysis following the same procedure as for the assemblage from the laboratory of Oberstockstall, to allow comparison between the results of both studies. Besides, as previously explained, the relatively standard combination of analytical techniques chosen for this project enabled a wider discussion including relevant published studies (cf. chapter 7).

6.3. Microscopic and analytical characterisation

6.3.1. Ore samples

Although arsenopyrite has previously been identified as the main ore for gold at the mining site of the Bockhart (Cech and Paar 1997; Cech and Walach 2001), it seems from the present analyses of ore specimens coming from the Bockhart and the Erzwies mining districts, and the Angertal smelting site, that there is a much wider variety of sulphidic minerals exploited, principally rich in pyrite, galena, and sphalerite, containing variable amounts of arsenopyrite and very small quantities of chalcopyrite, with a gangue composed of manganese-rich iron carbonate and quartz (Table 6.1, Fig. 6.16 to 6.19). Typical minor elements for these types of sulphidic ore, such as antimony (60-1230 ppm Sb), nickel (≤ 180 ppm Ni), titanium (20-890 ppm Ti), and barium (≤ 270 ppm Ba), have also been identified in various ranges. The former two probably attest to the presence of small pockets of fahlores, while the latter two constitute most likely part of the gangue minerals (Table 6.1). The analysis of a larger set of samples has shown that the content in silver – when detected – can vary greatly from one ore fragment to another, roughly ranging between 30 ppm and 0.4 wt% (Table 6.1). This seems to differ to some extent from initial results obtained from the analysis of a lower number of minerals, for which silver was detected in much lower concentrations (Mongiatti *et al.* in press). A few inclusions of fahlores have been noticed in several pieces of these ores. Despite using the 'Alloy' method for ED-XRF analysis (cf. chapter 3), no gold could be detected in any of these samples.

	Mg	Al	Si	S	Mn	Fe	Cu	Zn	As	Pb
	wt%	wt%	wt%	wt%	Wt%	wt%	wt%	wt%	wt%	wt%
AN 32/2/S1	7.6	2.0	27.6	4.5	b.d.l.	31.1	0.01	b.d.l.	27.1	0.0
AN 58/1/S1	b.d.l.	b.d.l.	b.d.l.	9.0	2.6	11.0	0.8	8.2	0.2	67.9
AN 60/1/S1	0.2	0.8	39.5	6.2	2.7	23.7	0.3	12.8	0.2	13.6
AN 64/2/S1	b.d.l.	b.d.l.	1.0	10.3	0.5	4.4	0.8	43.6	b.d.l.	39.2
AN 7/1/S1	2.2	0.6	23.0	13.9	b.d.l.	44.4	0.0	b.d.l.	15.5	0.1
AN 90/1/S2	0.3	0.3	22.1	15.6	b.d.l.	46.5	0.0	b.d.l.	14.7	0.4
BO 133-01/S2	b.d.l.	0.8	8.9	8.8	2.2	9.1	b.d.l.	0.0	0.0	70.1
BO 152-01/S2	3.7	6.5	39.5	4.6	0.2	18.9	0.7	7.0	16.4	2.2
BO 991/10/S1	b.d.l.	1.1	7.0	10.7	0.2	5.0	1.2	64.0	0.1	10.4
BO 991/11/S1	b.d.l.	0.7	9.4	9.9	0.8	9.2	2.5	51.1	0.2	15.7
BO 991/13/S1	b.d.l.	b.d.l.	b.d.l.	10.6	b.d.l.	0.4	0.2	4.5	0.0	83.8
BO 991/2/S1	b.d.l.	0.7	5.0	10.3	0.1	6.6	3.9	44.5	0.2	28.3
BO 991/3/S1	b.d.l.	0.5	8.6	11.4	0.5	8.2	3.7	63.6	0.3	2.8
BO N03/S2	0.8	0.7	4.3	3.8	11.8	41.1	0.1	5.4	0.0	31.8
ER S001/S2	1.6	0.3	0.6	0.6	25.0	71.7	b.d.l.	b.d.l.	0.0	0.0
ER S002/S2	b.d.l.	1.3	16.4	6.7	2.6	11.0	b.d.l.	0.1	0.0	61.7
ER S003/S2	b.d.l.	0.7	4.5	7.6	0.9	5.5	0.3	79.6	b.d.l.	0.3
ER S004/S2	0.4	1.0	9.7	4.6	12.1	34.5	0.0	10.0	b.d.l.	27.5
ER S005/S2	b.d.l.	b.d.l.	1.5	10.2	1.6	8.8	0.0	55.4	b.d.l.	22.0

	Ti	Cr	Ni	Ag	Cd	Sb	Ba
	ppm	ppm	ppm	ppm	ppm	ppm	ppm
AN 32/2/S1	235	240	b.d.l.	34	b.d.l.	74	37
AN 58/1/S1	33	b.d.l.	109	1470	345	797	b.d.l.
AN 60/1/S1	25	235	31	527	769	98	
AN 64/2/S1	57	b.d.l.	25	594	2014	218	b.d.l.
AN 7/1/S1	233	280	b.d.l.	31	b.d.l.	78	21
AN 90/1/S2	219	289	b.d.l.	111	b.d.l.	79	13
BO 133-01/S2	107	52	115	761	17	73	b.d.l.
BO 152-01/S2	888	167	47	160	285	67	267
BO 991/10/S1	219	88	6	345	3491	107	35
BO 991/11/S1	162	135	39	1303	2748	146	39
BO 991/13/S1	62	b.d.l.	119	3603	195	1230	b.d.l.
BO 991/2/S1	218	b.d.l.	62	1367	2096	313	38
BO 991/3/S1	193	156	92	438	3707	75	79
BO N03/S2	357	379	20	341	333	119	32
ER S001/S2	32	390	12	b.d.l.	b.d.l.	b.d.l.	13
ER S002/S2	134	101	166	589	23	61	14
ER S003/S2	282	123	178	45	5582	73	19
ER S004/S2	332	382	49	378	742	110	48
ER S005/S2	182	140	47	294	3200	104	b.d.l.

Table 6.1. *Bulk chemical composition of ore fragments from the Angertal (AN), the Bockhart (BO) and the Erzwies (ER) by ED-XRF ("Alloy method"; data normalised to 100 wt%; b.d.l.: below detection limit). Each of the values given here is the average of three consecutives runs. See appendix 4 for the full results.*

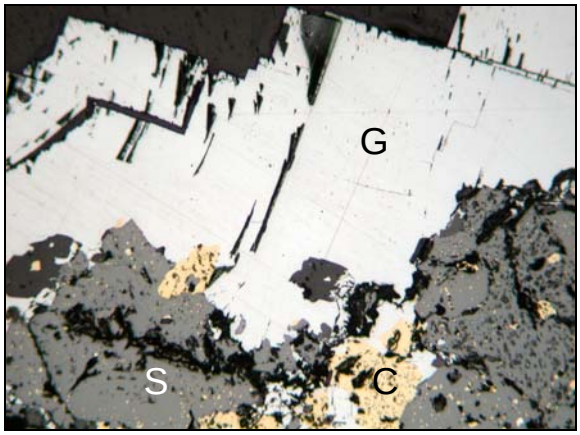
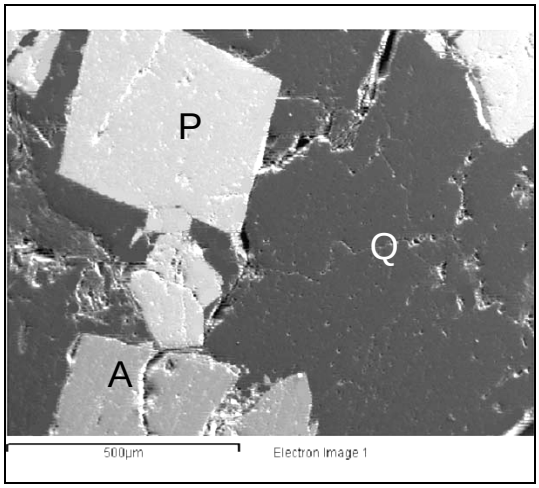


Fig. 6.16. *Photomicrograph of an ore fragment from the Bockhart mining site, showing crystals of galena (G), sphalerite (S), and chalcopyrite (C) (BO 991-07/S1, optical microscope, plane polarised light, 100x, long axis ~1 mm).*

Fig. 6.17. *Crystals of arsenopyrite (A) and pyrite (P) in a gangue of quartz (Q), from the Bockhart (BO 152-01/S1, SE, 100x).*



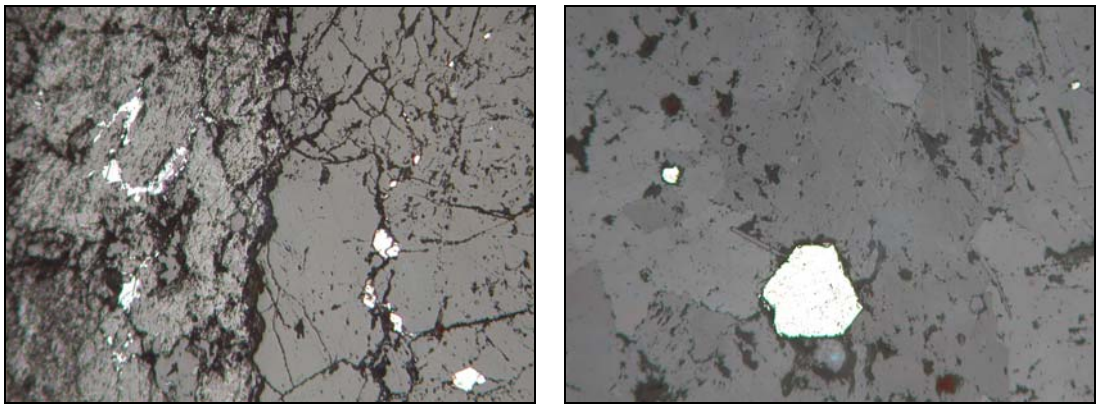


Fig. 6.18. *Ore fragments from the Erzwies showing bright crystals of galena and pyrite in a gangue of iron carbonate (medium grey) and quartz (dark grey) (optical microscope, plane polarised light, left: ER S002/S1, 100x, long axis ~850 µm; right: ER S004/S1, 100x, long axis ~1 mm).*

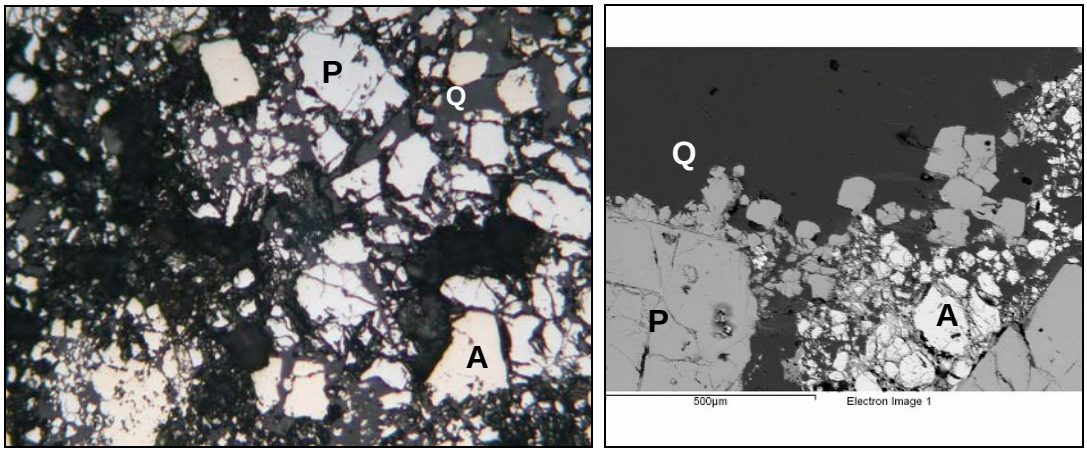


Fig. 6.19. *Photomicrographs of a piece of ore from the Angertal showing pyrite (P) and arsenopyrite (A) in a gangue of quartz (Q) (AN 90/1/S1; left: optical microscope, plane polarised light, 100x, long axis ~1 mm; right: BSE, 100x).*

The overall data obtained on the ore indicate that there were strong similarities between the minerals from all three sites. This appears as a relatively good match to historical sources, which attest to the exploitation of similar ore deposits at both mines between the fourteenth and sixteenth centuries. The fourteenth-century mining focused mostly on veins of quartz which contained native gold, while it seems that silver-bearing arsenopyrite intergrown with iron-rich minerals was the main ore mined in the fifteenth and sixteenth centuries (C. Bartels, *pers. comm.)*. Several ore samples analysed by Hauptmann and Rehren (1990) may reflect the late medieval period of activity, as they have observed small particles of native gold interspersed between quartz grains. The occurrence of a large variety of sulphidic ores in the sixteenth-century archaeological assemblages could initially appear different to the expected predominance of arsenopyrite. It seems, however, that although arsenopyrite was probably the main vein of the deposits at both mines, it may not represent the main mineral of the smelting operation. It is likely possible that the miners were aiming at recognisable pockets of specific sulphidic minerals, such as fahlores, which were particularly rich in precious metals, leaving behind the poor ones. The occurrence of fahlores in the ore deposits is suggested by the identification of trace elements, such as antimony and nickel, and the observation under the optical microscope of very small phases, which were most likely these complex sulphidic ores. A good illustration of such a situation is the example of a mine in the Harz mountains: its deposit has been described by modern mineralogy as polysulphidic, dominated by zinc, lead and copper; written sources report that the silver was

included in the galena; analytical studies have revealed that the silver was found concentrated in small particles or pockets of fahlores, which had grown within the main galena vein (C. Bartels, *pers. comm.)*. The ore dressing plant excavated in the Bockhart may further support this case, as crushing and grinding the ore to pieces of small size would have allowed the miners to carry out an efficient sorting and separate the worthy particles from the gangue. If a wider variety of minerals other than arsenopyrite was known to contain the precious metals, then the miners would be targeting these specifically, and this may explain the pattern of ores observed today.

6.3.2. Slag fragments

The bulk chemical compositions of the platy slag specimens, obtained by ED-XRF analysis, are dominated by iron oxide (34-56 wt% FeO) and silica (15-35 wt% SiO_2), and are mainly rich in alumina (2-6 wt% Al_2O_3) and the oxides of sulphur (2-17 wt% SO_3), manganese (1-11 wt% MnO), lead (0.3-16 wt% PbO), and zinc (1-7 wt% ZnO), with lower concentrations of soda (≤ 1 wt% Na_2O), potash (0.5-1.4 wt% K_2O), calcium oxide (1-3 wt% CaO), magnesia (0.1-1.5 wt% MgO), titanium oxide (0.1-0.2 TiO_2), and arsenic oxide (0.01-0.2 wt% As_2O_3) (Table 6.2). Several minor elements, such as nickel, antimony, strontium and thallium[4], already identified in the ore samples, can also be noticed in the slag (Table 6.2).

Most specimens contain some porosity but are overall relatively dense, as can be seen on several examples below (Fig. 6.20). The concentrations detected in slag fragments with higher sulphur content sum up to totals of around 106 wt% on average (Table 6.2). The analysis of these samples particularly rich in matte inclusions overestimate the amount of oxides, resulting in higher concentrations of most elements than expected. However, despite higher totals, these samples are generally highly porous, more than slag poor in sulphidic phases, due to sulphur dioxide bubbles which remained trapped during the solidification of the slag (Fig. 6.22). It is therefore necessary to combine this analytical data to the study of the

[4] Note that strontium and thallium were not included in Table 6.1, which presents the concentrations of elements detected using the "Alloy" method because the "Alloy" method is not set up to quantify either of them and they could only be detected with the "Turboquant" method, for which the results have not been included as they are not informative for the major elements (cf. chapter 3 for the description of the methods).

microstructure of each sample to understand the reason for these variations in analytical results.

	Na_2O wt%	MgO wt%	Al_2O_3 wt%	SiO_2 wt%	SO_3 wt%	K_2O wt%	CaO wt%	TiO_2 wt%	MnO wt%	FeO wt%	CuO wt%	ZnO wt%	PbO wt%
AN 113-01/S2	b.d.l.	1.3	4.8	29.3	1.5	1.4	3.4	0.2	4.1	33.6	0.4	4.1	15.6
AN 113-03/S2	b.d.l.	1.4	4.4	28.9	5.4	1.2	2.2	0.2	6.4	39.4	0.4	5.7	4.3
AN 113-04/S2	b.d.l.	1.4	4.7	26.3	2.8	1.3	2.5	0.2	8.1	43.6	0.5	3.1	5.2
AN 117-01/S2	b.d.l.	0.1	1.7	16.2	17.0	0.5	0.5	0.1	2.4	49.6	1.1	7.4	3.4
AN 117-02/S2	b.d.l.	0.1	1.6	15.4	16.7	0.5	0.6	0.1	2.3	47.2	1.7	7.0	6.6
AN 130-01/S2	b.d.l.	1.5	4.8	24.8	3.8	1.1	2.7	0.2	11.3	40.4	0.3	4.0	5.0
AN 130-10/S2	b.d.l.	1.5	4.5	24.3	4.1	1.1	2.6	0.2	11.2	40.5	0.3	4.2	5.3
AN 134a-01/S2	b.d.l.	1.3	5.9	28.2	4.0	1.4	2.9	0.2	7.5	40.4	0.4	3.8	3.9
AN 134a-02/S2	1.1	1.3	4.2	25.8	2.7	1.1	2.4	0.2	7.8	42.3	0.4	1.3	9.1
AN 134b-01/S2	b.d.l.	0.2	1.7	16.8	15.2	0.5	0.6	0.1	2.6	51.2	0.8	7.3	2.9
AN 148-01/S2	b.d.l.	0.6	3.2	20.9	8.4	0.8	1.0	0.1	2.5	56.0	1.2	2.3	2.9
AN 170-03/S2	1.2	0.6	4.8	30.9	5.4	1.1	1.2	0.2	1.4	50.4	0.4	1.4	0.9
AN 187-02/S2	0.7	0.8	4.5	34.7	5.6	1.0	1.5	0.2	2.1	47.6	0.1	0.8	0.3
Average	**0.2**	**0.9**	**3.9**	**24.8**	**7.1**	**1.0**	**1.9**	**0.2**	**5.4**	**44.8**	**0.6**	**4.0**	**5.0**

	NiO ppm	As_2O_3 ppm	SrO ppm	Ag ppm	CdO ppm	Sb ppm	Ba ppm	Tl ppm	Total* wt%
AN 113-01/S2	68	1102	372	b.d.l.	b.d.l.	569	464	262	91.0
AN 113-03/S2	40	312	218	39	11	105	366	71	99.3
AN 113-04/S2	58	1083	236	15	b.d.l.	125	336	72	97.3
AN 117-01/S2	b.d.l.	171	82	161	61	100	173	14	111.3
AN 117-02/S2	10	261	104	279	494	149	165	90	105.9
AN 130-01/S2	102	326	213	32	b.d.l.	57	270	59	97.2
AN 130-10/S2	108	761	216	42	b.d.l.	52	262	74	96.6
AN 134a-01/S2	12	722	302	22	b.d.l.	79	442	44	98.4
AN 134a-02/S2	36	2128	295	26	b.d.l.	200	285	175	95.2
AN 134b-01/S2	b.d.l.	178	78	139	25	94	175	23	108.2
AN 148-01/S2	b.d.l.	142	131	79	b.d.l.	81	335	25	101.5
AN 170-03/S2	b.d.l.	326	109	23	b.d.l.	23	238	b.d.l.	101.1
AN 187-02/S2	b.d.l.	185	104	31	b.d.l.	b.d.l.	220	b.d.l.	98.6
Average	**b.d.l.**	**590**	**190**	**70**	**b.d.l.**	**125**	**290**	**70**	

** These values represent totals of detected concentrations before normalisation.*

Table 6.2. *Bulk chemical composition of slag fragments by ED-XRF ("Turboquant" method; data normalised to 100 wt%; b.d.l.: below detection limit). Each of the values given here is the average of three consecutives runs.*

The microstructure of this slag is generally very homogeneous and typical of tapped slag, with a glass matrix and numerous crystals of iron-rich olivines (42-65 wt% FeO, 27-36 wt% SiO_2), containing various amounts of zinc oxide (1-5 wt%

ZnO), manganese oxide (4-18 wt% MnO), magnesia (1-6 wt% MgO), alumina (1-3 wt% Al_2O_3), and lower quantities of potash (1 wt% K_2O) and calcium oxide (1 wt% CaO), as shown by SEM-EDS analysis. These olivine crystals are usually highly acicular, and oriented perpendicular to the direction of the cooling front (Fig. 6.20 and Fig. 6.22, right). This, together with the flow texture exhibited by some of the slag fragments, confirms that the slag had a relatively low viscosity and was tapped out of the furnace, where it solidified fairly quickly.

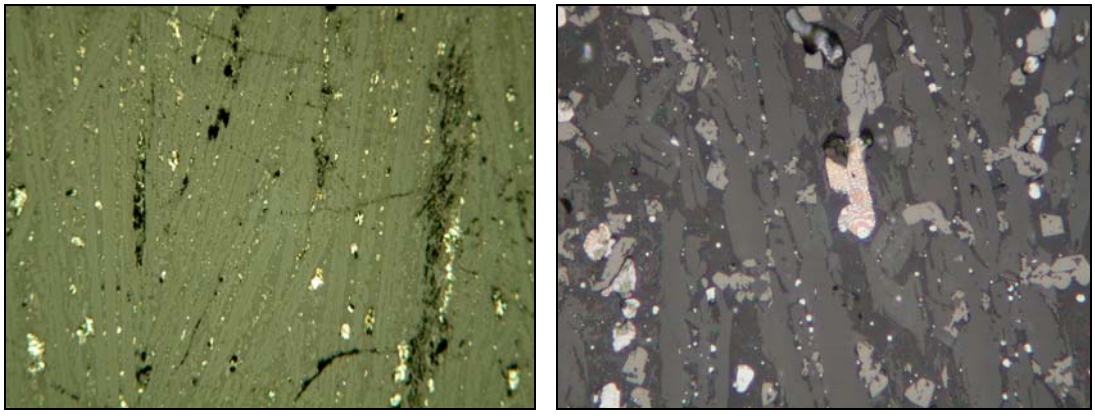


Fig. 6.20. *Photomicrographs of typical platy slag samples, showing the acicular fayalitic crystals in a glass matrix. Note the numerous bright inclusions of matte in various sizes, and the abundance of magnetite crystals (light brown) in the image on the right (optical microscope, plane polarised light, left: AN 150-09/S1, 100x, long axis ~1 mm; right: AN 134a-02/S1, 500x, long axis ~200 µm).*

The slag fragments analysed also present spinel crystals of magnetite, preferentially enriched in alumina (8-13 wt% Al_2O_3), zinc oxide (4-7 wt% ZnO), manganese oxide (5-6 wt% MnO) and titanium oxide (1 wt% TiO_2) (SEM-EDS data), along with many inclusions of matte (Fig. 6.21). These matte phases included in the slag principally consist of sulphidic compounds of lead, iron, zinc, copper, and arsenic associated in various proportions (PbS, $Cu_xFe_yS_z$, $Zn_xFe_yS_z$, etc.). EPMA-WDS analysis showed one sample with a sulphidic phase particularly rich in arsenic, iron, copper, and nickel and containing silver and gold in relatively high concentrations (Table 6.3, AN 170-03/S1). This phase may have formed from the high-temperature reaction of different sulphidic minerals during the melt or be a partly melted and half-reacted fahlore inclusion. Similarly, 0.2 wt% of gold have been detected in lead sulphide, and 0.1 wt% of silver with 0.2 wt% of gold in a zinc-iron sulphide in two other samples (Table 6.3, AN 130-01/S1 and AN 150-09/S1, EPMA-WDS). The proportion of matte phases included in platy slag layers can vary

greatly from one sample to another (Fig. 6.22). One specific sample (AN 117-01/S1) even appears to have no glass matrix but matte phases in between olivine crystals instead (Fig. 6.22). This range of matte concentrations in slag seems to depend on the finding location of the slag fragment (Fig. 6.5), and tends to decrease from furnace 1 to furnace 3. This could illustrate either a variation in the smelting process itself from one batch to another in terms of temperature and redox conditions in the furnace, or a possible use of the three furnaces in series rather than simultaneously in parallel. This aspect of the smelting operation will be discussed in greater detail in the next chapter.

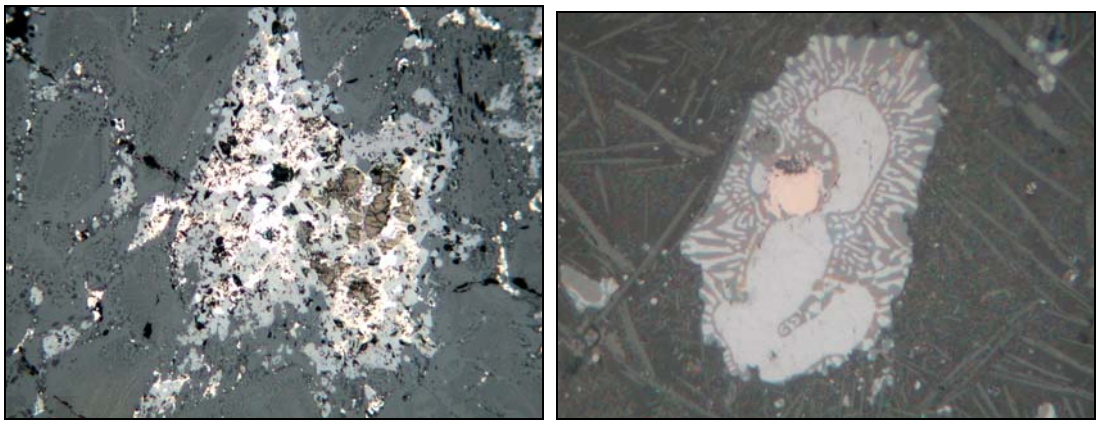


Fig. 6.21. *Detail of matte inclusions within slag phases, composed of a mixture of different sulphides. Note the partial oxidation to magnetite (light brown) on the left picture, and the bright orange copper prill in the middle of the matte inclusion on the right picture (optical microscope, plane polarised light, left: AN 117-02/S1, 200x, long axis ~500 µm; right: AN 113-01/S1, 1000x, long axis ~100 µm).*

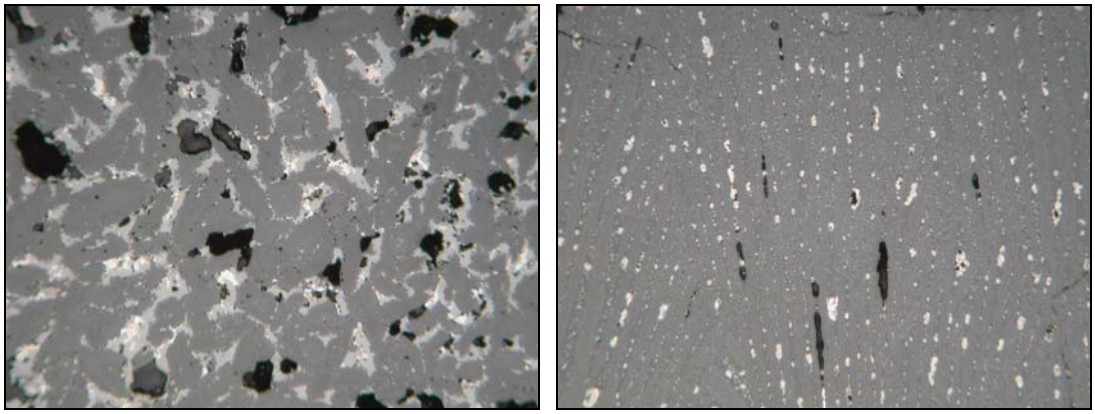


Fig. 6.22. *Two samples of platy slag showing a difference in volume in their slag/matte inclusions ratio, one coming from a stratigraphic layer in front of furnace 1 (left, AN 117-01/S1) and the other from an area in front of furnace 3 (right, AN 113-02/S1) (optical microscope, plane polarised light, 100x, long axis ~1 mm).*

Prills appear occasionally entrapped in the slag phase (Fig. 6.23). These are mainly composed of lead (80-90 wt% Pb), with a thin superficial oxide layer (*ca.* 5-10 wt% O). Many of these prills have a fairly high silver content (1-4 wt% Ag). Optical microscopy and spot analyses by EPMA-WDS revealed that this silver is either found associated with gold (Table 6.3) or combined to antimony in the form of discrete islands of dyscrasite (Ag_3Sb) in a metallic lead matrix, which can display up to a few percent of gold as well (3 wt% Au; AN 134a-02/S1). Gold has also been detected in several other lead prills in slag (0.5 wt% Au; AN 117-02/S1; SEM-EDS), usually associated with silver, such as in one specimen of channel slag (Table 6.3, AN 187-02; EPMA-WDS). Silver has also been identified in an oxidised arsenic-rich lead prill, probably a speiss inclusion (Table 6.3, AN 134a-03/S1; EPMA-WDS).

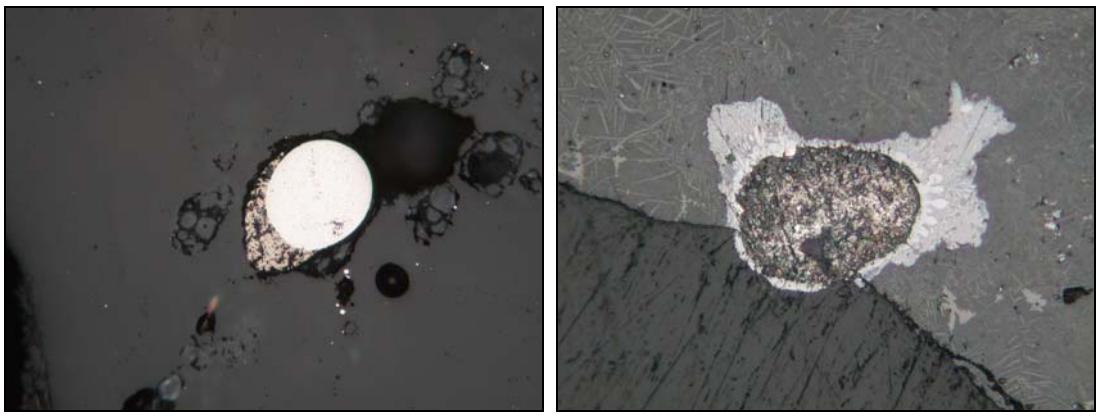


Fig. 6.23. *Bright lead-rich prills trapped in slag layers. Note the surrounding matte in both (optical microscope, plane polarised light, left: AN 157-05/S1, 100x, long axis ~1 mm; right: AN 113-01/S1, 200x, long axis ~500 µm).*

	Type of inclusion	S wt%	Mn wt%	Fe wt%	Cu wt%	Zn wt%	As wt%	Ag wt%	Sb wt%	Au wt%	Pb wt%	Total wt%
AN 170-03/S1	Matte	18.4	0.1	23.5	15.9	0.1	27.6	0.4	0.3	0.03	13.7	105.2
AN 130-01/S1*	Matte	37.4	1.1	29.1	1.8	26.6	b.d.l.	0.1	0.03	0.1	3.8	97.1
AN 150-09/S1*	Matte	38.6	0.4	24.6	10.5	25.6	0.1	0.1	0.03	0.1	0.1	97.5
AN 187-02/S1	Prill	4.8	0.1	b.d.l.	0.2	b.d.l.	b.d.l.	67.0	6.7	2.4	18.8	101.0
AN 134a-03/S1	Prill	0.3	b.d.l.	22.4	3.7	1.6	27.5	0.8	0.3	b.d.l.	43.4	62.5

** Averages calculated out of 2 EPMA-WDS analyses.*

Table 6.3. *Spot analyses by EPMA-WDS of various matte phases and prills included in the slag and containing silver and gold (data normalised to 100%; b.d.l.: below detection limit). Last column: totals before normalisation.*

Sample AN 134a-03/S1, which has not been analysed by ED-XRF, is of particular interest due to its various compositional phases, which show both the initial raw material and the forming slag: large areas of galena, some slag with numerous inclusions and areas where the raw materials seem to have only half-reacted can be noticed (Fig. 6.24). This particular sample is rich in arsenic in the silicate matrix, comparatively to the others, with high local concentrations (13 wt% As_2O_3, SEM-EDS). Its bulk is mostly composed of lead silicate (59 wt% PbO, 20 wt% SiO_2), with zinc oxide (10 wt% ZnO), iron oxide (4 wt% FeO), and arsenic oxide (3 wt% As_2O_3). Its microstructure displays arsenic-rich lead prills (Table 6.3). It is interesting to note that this sample, which has not fully reacted, is precisely the one showing a higher concentration in arsenic. It raises the question of the extent to which the arsenic in fully reacted samples would have burnt off, therefore not being detected in typical slag samples from this site. This sample may, however, only show that arsenopyrite was probably not the main mineral smelted in the Angertal, as it has been observed that only small quantities of arsenic are lost during smelting so long as there is sulphur present in the system, as sulphur would oxidise and therefore vaporise before arsenic (Thornton *et al.* 2009).

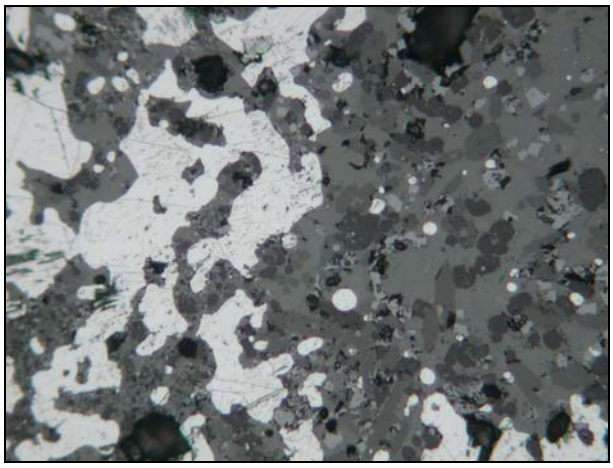


Fig. 6.24. *Mixture of galena (bright, left), which has partially reacted, and forming slag (right), showing a glassy matrix (medium grey) with various inclusions (AN 134a-03/S1, optical microscope, plane polarised light, 200x, long axis ~500 µm).*

6.3.3. Matte layer

The bulk composition of almost all the matte samples analysed by ED-XRF[5] revealed high concentrations of iron (37-56 wt% Fe), copper (18-25 wt% Cu), lead

[5] Matte AN 15-01/S2 is discussed separately below and has therefore not been included in the data presented here.

(14-28 wt% Pb) and sulphur (11-13 wt% S) with lower amounts of zinc (0.2-3 wt% Zn), silver (0.4-0.7 wt% Ag), arsenic (0.1-0.4 wt% As), antimony (0.01-0.1 wt% Sb) and nickel (0.01-0.1 wt% Ni). Silicon, manganese, chromium, and titanium are also present as small quantities of silica (0-2.4 wt% SiO_2), manganese oxide (0.1-0.4 wt% MnO), chromium oxide (0.04 wt% Cr_2O_3), and titanium oxide (0.01-0.03 TiO_2) (Table 6.4). Barium was detected in minute amounts and was therefore not included in the table below (≤ 30 ppm Ba).

	Si	S	Ti	Cr	Mn	Fe	Ni	Cu	Zn	As	Ag	Sb	Pb
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
AN 15-01/S2	0.3	13.3	0.01	0.04	0.7	74.0	b.d.l.	3.4	3.4	0.3	0.2	0.02	4.2
AN 88-01/S2	b.d.l.	10.5	0.01	0.03	0.1	56.2	0.1	20.5	0.2	0.1	0.7	0.01	16.1
AN 104-01/S2	1.5	11.1	0.03	0.03	0.3	36.9	0.01	18.2	2.9	0.2	0.5	0.1	28.2
AN 108-04/S2	b.d.l.	13.4	0.02	0.03	0.2	40.4	0.03	24.9	2.2	0.4	0.5	0.1	17.6
AN 108-05/S2	b.d.l.	12.3	0.01	0.03	0.2	46.1	0.04	22.9	2.3	0.3	0.4	0.1	15.2
AN 108-06/S2	0.3.	12.5	0.01	0.03	0.3	47.3	0.04	22.2	2.3	0.3	0.4	0.1	14.3
AN 108-07/S2	b.d.l.	11.9	0.01	0.03	0.3	47.0	0.1	20.4	2.7	0.3	0.4	0.1	16.7
Average*	**0.3**	**12.0**	**0.02**	**0.03**	**0.2**	**45.7**	**0.05**	**21.5**	**2.1**	**0.3**	**0.5**	**0.1**	**18.0**

** Averages calculated excluding sample AN 15-01/S1*

Table 6.4. *Bulk chemical composition of matte fragments by ED-XRF ("Alloy" method; data normalised to 100 wt%; b.d.l.: below detection limit). Each of the value given here is the average of three consecutives runs.*

These matte cakes are structurally composed of a complex mixture of different sulphidic phases, mainly pyrrhotite, which results from the partial burning of pyrite during the melt. Also present are lead sulphide, complex iron-copper sulphides of various compositions (20-50 wt% Fe, 10-45 wt% Cu, 25-35 wt% S, SEM-EDS) and iron-zinc sulphides (37 wt % Fe, 27 wt% Zn, 2 wt% Cu, 34 wt% S, SEM-EDS). Some of these sulphides such as lead sulphide or pyrrhotite have partly further oxidised, to form crystals of lead sulphate and magnetite (Fig. 6.25 to 6.27). Magnetite usually includes most of the manganese oxide, alumina and titanium oxide identified by ED-XRF in the samples, as well as some oxidised copper, zinc, and lead in several samples. In the few specimens where silica has been detected, it is found in fayalitic slag inclusions. One sample also displays some half-reacted gangue material mainly composed of iron carbonate (AN 88-01/S1, Fig. 6.28).

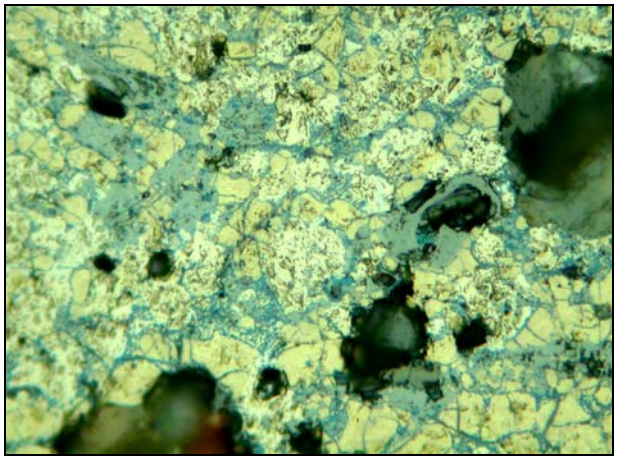


Fig. 6.25. *Typical microstructure of a matte layer (AN 198-01/S1, optical microscope, plane polarised light, 100x, long axis ~1 mm).*

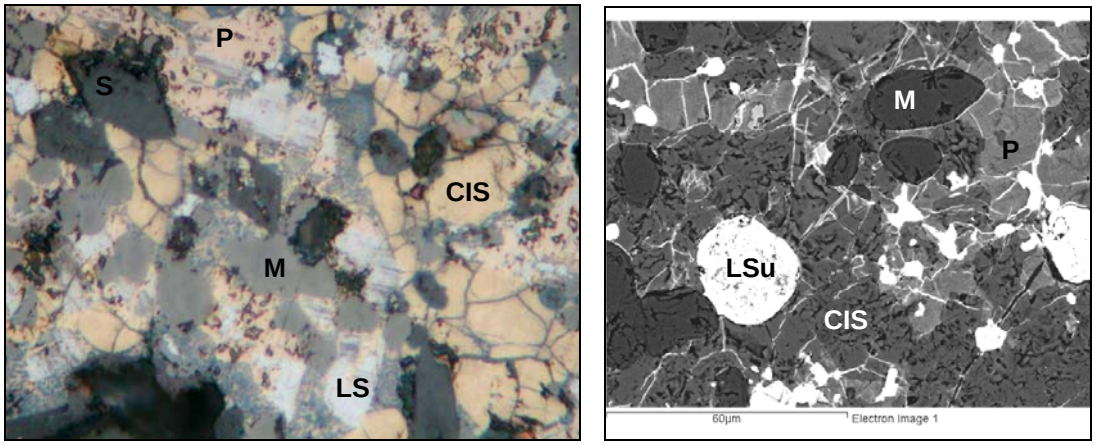


Fig. 6.26. *Detail of the microstructure of two different pieces of matte, exhibiting phases of magnetite (light brown, M), pyrrhotite (light cream, P), a complex copper-iron sulphide (yellow, CIS), lead sulphate(LSu), which has formed from the corrosion of lead sulphide (white, LS), and copper sulphide (blue), which has probably formed as a secondary phase and deposited in cracks and grain boundaries during burial. Note the slag inclusion (dark grey, S) on the left picture (left: AN 104-04/S1, optical microscope, plane polarised light, 1000x, long axis ~100 µm; right: AN 108-06/S1, BSE, 1000x).*

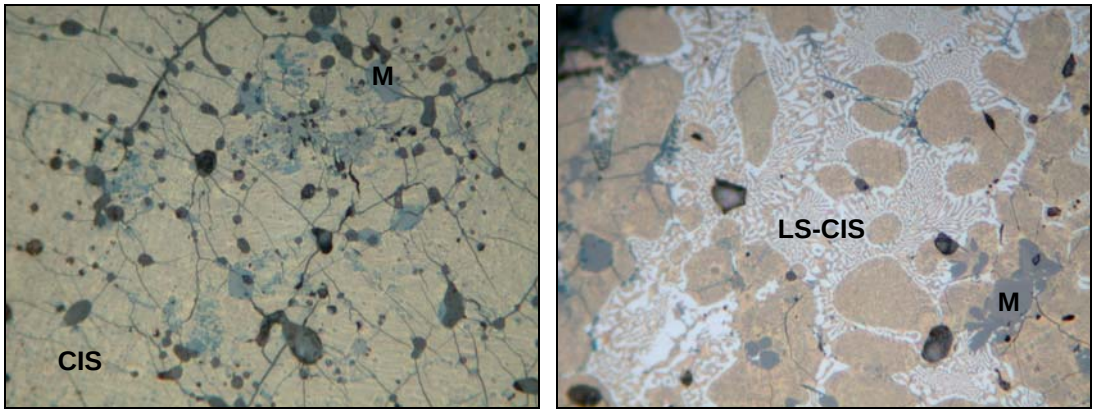


Fig. 6.27. *Further example of characteristic matte microstructure, showing the formation of magnetite (light brown, M) from the main sulphidic phases (yellow with flesh-coloured stripes, CIS) and a eutectic mixture of lead sulphide (LS) with copper-iron sulphide, forming in between dendrites of a mixture of copper-iron sulphides (AN 108-02/S1, optical microscope, plane polarised light, 500x, long axis ~200 µm).*

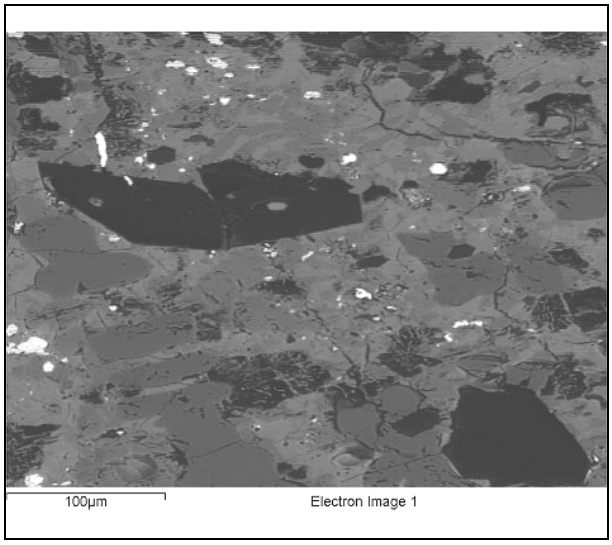


Fig. 6.28. *Dark crystals of partially reacted iron-carbonate gangue in a matte matrix (AN 88-01/S1, BSE, 300x).*

High concentrations of silver are regularly detected in several of these sulphides, such as lead sulphide phases now corroded to lead sulphate (1-4 wt% Ag, SEM-EDS) and/or copper-iron sulphide phases (Table 6.5). These matte samples also show lead prills trapped in their bulk, which contain relatively significant quantities of precious metals and have most often partially corroded to lead oxide (Fig. 6.29). These prills are mainly composed of lead (75-90 wt% Pb) with a thin superficial oxide layer (10-13 wt% O). Many of these have fairly high silver content (2-4 wt% Ag) associated to antimony (1-2 wt% Sb), similarly to the prills trapped in the slag,

	S wt%	Fe wt%	Cu wt%	Ag wt%
AN 15-01/S1	26.4	25.7	46.7	1.2
AN 88-01/S1 (*)	36.2	16.6	46.1	1.1
AN 88-02/S1	30.4	14.3	54.5	0.8
AN 108-01/S1	31.9	15.3	52.0	0.8
AN 108-02/S1	30.2	14.8	54.3	0.7
AN 108-06/S1	29.3	14.7	55.0	1.0
Average	**30.7**	**16.9**	**51.4**	**1.0**

Table 6.5. *Silver-rich copper-iron sulphide phases analysed by SEM-EDS (EPMA-WDS analysis indicated by *) (data normalised to 100 wt%).*

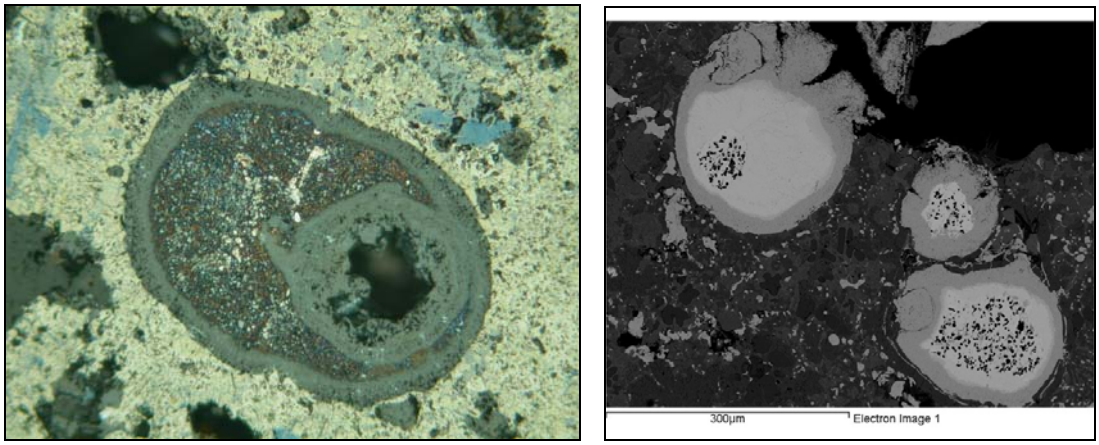


Fig. 6.29. *Examples of lead prills in matte samples: metallic lead is surrounded by lead sulphate formed from the corrosion of lead sulphide. The numerous dark particles noticeable in bright metallic lead come from the abrasive silicon carbide powder of the polishing cloth. (AN 108-01/S1; left: optical microscope, plane polarised light, 200x, long axis ~500 µm; right: BSE, 200x).*

According to the ED-XRF analysis, matte AN 15-01 seems to differ slightly from the main set of specimens in that it is mostly composed of iron (74 wt% Fe) with higher levels of zinc and manganese oxide (3 wt% Zn, 0.9 wt% MnO), and smaller amounts of lead and copper (4 wt% Pb, 3 wt% Cu) (Table 6.4). This matte appears to be more corroded than the other matte cakes, and mostly composed of pyrrhotite and magnetite, probably formed during the smelting of a pyrite-rich raw material (Fig. 6.30). SEM-EDS analysis, however, shows that in non-corroded areas, the microstructure of this specific matte is very similar to that of the rest of the samples, particularly with the identification of the silver-rich copper-iron sulphide (1.2 wt% Ag) and oxidised lead prills.

This matte may reflect either different redox conditions in the furnace or the processing of a different mixture of ores. However, it is on the whole corroded and has been found away from the furnaces and the main waste deposit (Fig. 6.5); it may therefore be regarded as an exception and is probably not representative of the whole site.

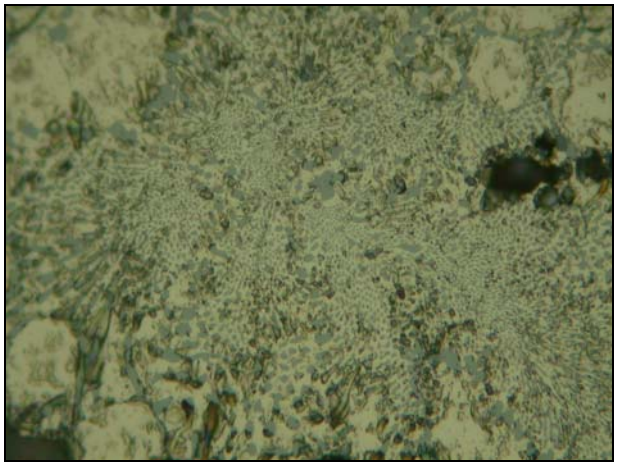


Fig. 6.30. *Large area of eutectic mixture of pyrrhotite (light cream-coloured phase) and magnetite (light brown), which has formed from the oxidation of iron-rich sulphides (AN 15-01/S1, optical microscope, plane polarised light, 500x, long axis ~200 µm).*

6.3.4. Furnace wall

The ED-XRF analysis of a non-vitrified area of furnace wall fragment (Fig. 6.12, p.199) shows that the chemical composition of this material is mostly silica (70 wt% SiO_2) and alumina (18 wt% Al_2O_3), with smaller amounts of soda (5 wt% Na_2O), potash (3 wt% K_2O), iron oxide (2 wt% FeO), lime (1 wt% CaO), and magnesia (1 wt% MgO), as well as traces of titanium oxide, phosphates, sulphur oxide, manganese oxide, barium and zinc oxide (Table 6.6). On the other hand, the analyses of various areas of vitrified ceramic show relatively lower amounts of silica and soda, and higher concentrations of iron oxide, potash, lime, and magnesia especially towards the surface (Table 6.6). Soda and potash are unusually high for a non-vitrified ceramic and may be due to contamination from the fuel ash and/or because there are some molten feldspars, i.e. potassium or sodium aluminium silicates ($(K,Na)AlSi_3O_8$), in the ceramic matrix.

A polished cross-section of a slagged area of the same piece of furnace wall reveals that this silica-rich fabric has melted and vitrified to form a more homogeneous glass, with residual crystals of quartz or feldspar (Fig. 6.31) and zircon, newly formed dendrites of magnetite close to the surface (Fig. 6.32) as well

as separate inclusions of lead-rich iron sulphide (58 wt% Fe, 7 wt% Pb, 1 wt% Cu, 34 wt% S; Fig. 6.33).

	Na_2O wt%	MgO wt%	Al_2O_3 wt%	SiO_2 wt%	P_2O_5 wt%	SO_3 wt%	K_2O wt%	CaO wt%	TiO_2 wt%	MnO wt%	FeO wt%	ZnO wt%	BaO wt%
ED-XRF analysis of non-vitrified ceramic	4.8	0.8	17.9	70.0	0.2	0.1	3.0	1.0	0.3	0.1	1.7	0.1	0.1
SEM-EDS area analysis of vitrified ceramic	3.7	0.8	20.3	64.8	b.d.l.	b.d.l.	6.8	0.7	0.4	0.2	2.3	b.d.l.	b.d.l.
SEM-EDS area analysis of vitrified ceramic	3.7	2.6	26.0	55.5	b.d.l.	b.d.l.	4.6	1.2	1.0	b.d.l.	5.3	0.1	0.3
SEM-EDS area analysis of vitrified ceramic close to inner surface	2.2	1.2	14.1	61.8	b.d.l.	b.d.l.	5.0	3.1	0.7	0.5	10.6	0.7	0.2

Table 6.6. *Chemical composition of the ceramic fabric of a fragment of furnace wall ("Turboquant" method for the ED-XRF analysis; data normalised to 100 wt%; b.d.l.: below detection limit). Each of the values of the ED-XRF analysis given here is the average of three consecutives runs*

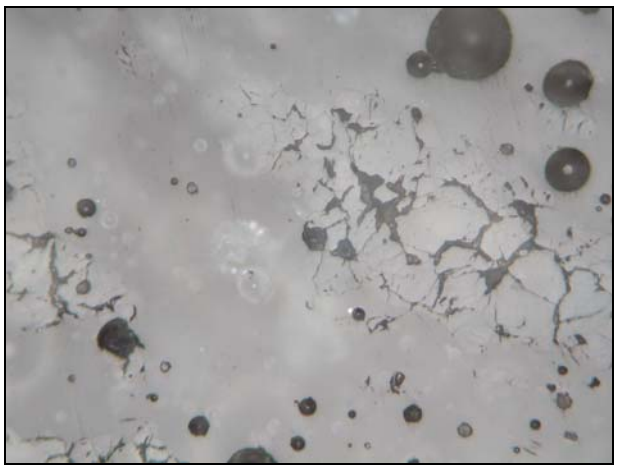


Fig. 6.31. *Vitrified ceramic matrix with residual quartz grains, which have partially reacted (AN 163-01/S1, optical microscope, plane polarised light, 100x, long axis ~1 mm).*

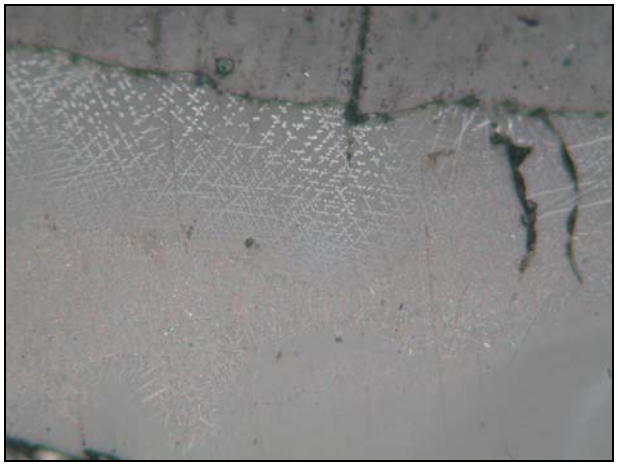


Fig. 6.32. *Slag on top of the ceramic. Note the numerous dendrites of magnetite, indicative of the richness of the glass in iron oxide and the locally oxidising conditions in that area of vitrification (AN 163-01/S1, optical microscope, plane polarised light, 200x, long axis ~500 µm).*

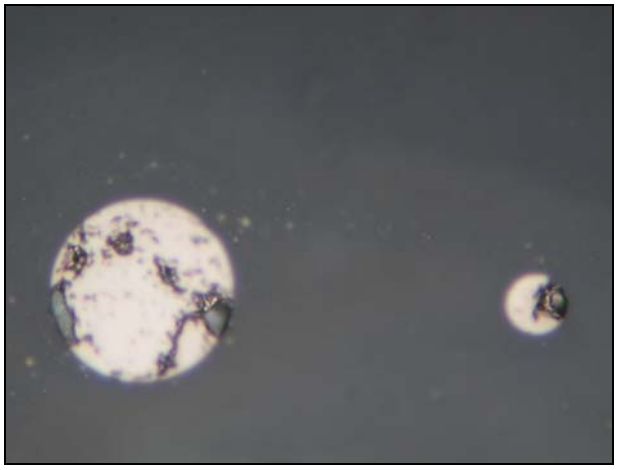


Fig. 6.33. *Inclusions of iron sulphide in the slag on top of the ceramic (AN 163-01/S1, optical microscope, plane polarised light, 500x, long axis ~200 µm).*

6.3.5. Furnace bottom

Several samples forming a complete vertical section of a furnace bottom have been prepared as polished cross-sections (Fig. 6.13, p.201 and 6.34). These specimens (AN N01/S1 to S8) include geological material at the bottom (Fig. 6.38), above which can be found layers of metallic lead (Fig. 6.37), matte (Fig. 6.36), and slag (Fig. 6.35-6.36). The upper part of this composite block of agglomerated materials is mostly composed of corrosion products. The proportion in volume of these phases on this particular section seems to be an approximately equal amount of lead and matte produced for 2 to 3 times more slag. This furnace bottom is a unique find and these ratios cannot however be considered as representative of a typical smelting operation for this site.

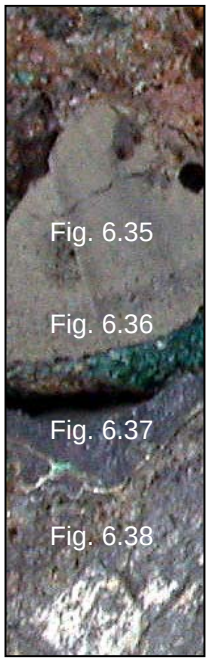


Fig. 6.34. *Close-up view of the furnace bottom section (AN N01).*

The bottom part of this section consists of a piece of solid rock, which is likely to be the stone base of the furnace. Most of this geological find is composed of quartz, plagioclase ($(Na,Ca)(Si,Al)_4O_8$), and alkali feldspar, as shown by relatively large areas of crystals of orthoclase ($KAlSi_3O_8$). Heavier phases of lead, matte, and slag can be seen to have penetrated into the cracks of this rock (Fig. 6.13, p.201 and 6.38). The slag is a typical fayalitic slag with many olivine crystals in a glass matrix (Table 6.7)

and numerous matte inclusions (Fig. 6.35). The matte is mostly composed of iron, lead, copper, and zinc, the balance being sulphur and oxygen, indicating that some sulphidic phases are oxidised (Table 6.8). The microstructure of the matte is divided into zinc-rich sulphides, cubanite-like phases and eutectoids of copper-rich sulphide (54 wt% Cu, 15 wt% Fe, 31 wt% S) and lead sulphide, now partially oxidised to lead sulphate (Table 6.8, Fig. 6.36).

Lead metal is usually found in association with copper sulphide, partially oxidised to copper sulphate (Fig. 6.37). The analysis of this metallic lead by EPMA-WDS revealed that it locally contains antimony (0.3-2.9 wt% Sb), silver (0.2-10.8 wt% Ag), and gold (up to 0.8 wt% Au). Silver and antimony can be found as dyscrasite (Ag_3Sb), as seen in the lead phases of most of the other samples of slag and matte; these phases can include 6-7 wt% gold.

	MgO	Al_2O_3	SiO_2	SO_3	K_2O	CaO	MnO	FeO	CuO	ZnO	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Slag glass matrix[(1)]	b.d.l.	10.0	45.0	2.0	3.0	2.0	1.0	24.0	1.0	7.0	5.0
Olivine crystals[(2)]	3.0	b.d.l.	30.0	b.d.l.	b.d.l.	b.d.l.	4.0	54.0	b.d.l.	9.0	b.d.l.

Table 6.7. *Chemical composition of the glass matrix of the slag and of the olivine crystals it contains; area of the furnace bottom (data normalised to 100 wt%; b.d.l.: below detection limit) (1): ED-XRF analysis, each value is the average of three consecutive runs ; (2): SEM-EDS spot analysis.*

	O	S	Fe	Cu	Zn	Pb
	wt%	wt%	wt%	wt%	wt%	wt%
Matte bulk[(1)]	11.0	24.0	33.0	11.0	10.0	11.0
Zinc-rich sulphides[(2)]	b.d.l.	35.0	14.0	b.d.l.	51.0	b.d.l.
Cubanite-like phase[(2)]	b.d.l.	35.0	38.0	22.0	5.0	b.d.l.

Table 6.8. *Chemical composition of the bulk and phases of the matte (data normalised to 100 wt%; b.d.l.: below detection limit). (1): ED-XRF analysis, each value is the average of three consecutive runs ; (2): SEM-EDS spot analysis.*

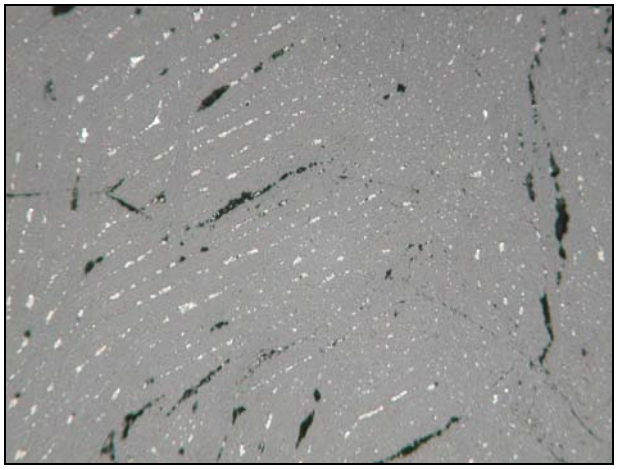


Fig. 6.35. *Typical fayalitic slag with bright inclusions of matte in between crystals of olivines, similar to most analysed samples of platy slag (AN N01/S7b, optical microscope, plane polarised light, 100x, long axis ~1 mm).*

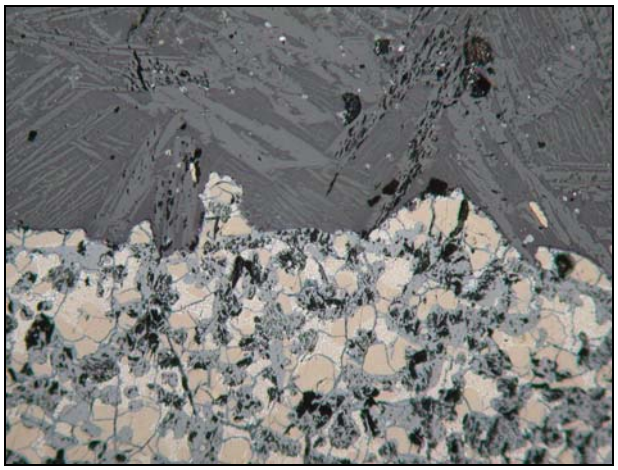


Fig. 6.36. *Interface matte (bottom)/ slag (top): light grey olivine crystals in a dark glass matrix on top of iron-rich sulphides (cream/light pink) partially oxidised to magnetite (light brown/grey) (AN N01/S6, optical microscope, plane polarised light, 100x, long axis ~1 mm).*

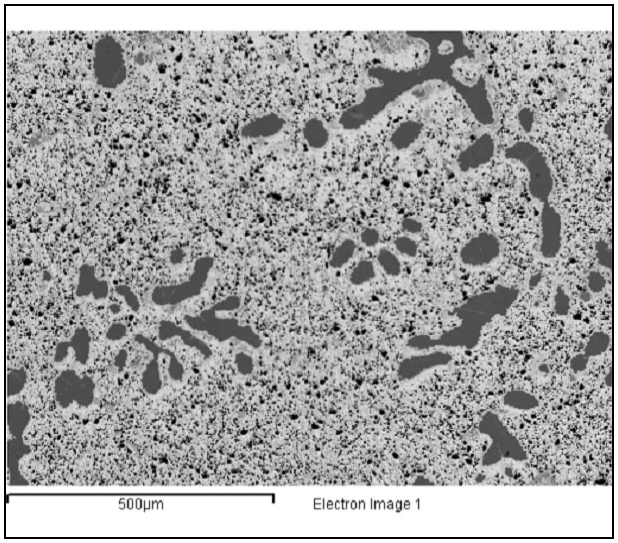


Fig. 6.37. *Layer of silver-rich metallic lead (white with black spots of silicon carbide particles) and dendrites of copper sulphide (dark grey) (AN N01/S1, BSE, 100x).*

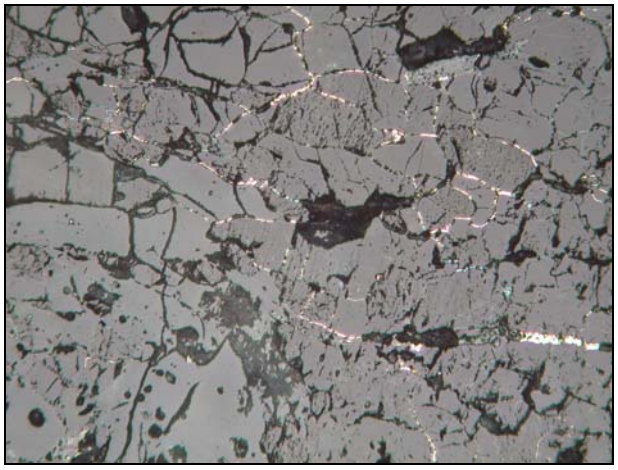


Fig. 6.38. *Geological material at the bottom of the section with bright sulphidic phases at the grain boundaries (AN N01/S1, optical microscope, plane polarised light, 100x, long axis ~1 mm).*

6.3.6. Summary

The two initial sections of this chapter have thoroughly described, both on macroscopic and microscopic levels, the various raw materials, waste products and other relevant pieces of evidence, which inform about the metallurgical processes carried out at the site. These results will be discussed and interpreted later on in this chapter. The analysis and study of the microstructure of fragments of ore, slag, matte, and to a lesser extent ceramic have shown that a wide variety of sulphidic ores typical of the region, such as galena, pyrite, sphalerite, arsenopyrite, chalcopyrite and also some fahlores, seems to constitute the body of minerals for the mining sites and potentially raw materials for the Angertal smelting site. Most of these ores display a relatively high quantity of silver but no gold at detectable levels. The furnace wall exhibits characteristic vitrification from high temperature and on its surface an enrichment in iron oxide from reactions with the charge. Slag shows the typical structure of fayalitic slag and matte is rich in copper and iron, as would be expected from the processing of a mixture of minerals such as described above. The waste product matte displays relatively high contents of silver and some gold detected sporadically, in various sulphides and in lead prills trapped among the sulphur-rich phases, and in the furnace bottom. In an attempt to see whether these concentrations could have been identified by the contemporary metallurgists, it was decided to subject several matte and lead samples to traditional cupellation experiments.

The following section will first explain the method used for the cupellation of archaeological samples of lead metal and matte, and then present details of the analysis of the used cupels and resulting gold-silver alloys from this operation. The

experimental aspect of this project intends to shed light on the economic value of the processed ores, by informing on the relative proportion of precious metals in the gold-silver bead. The cupellation of matte will also indicate the relative loss in precious metals in this phase, and whether it would have been worth processing it further. This could have been done by adding it to the charge in ulterior smelting, in order to recover its content of gold and silver. Another possible treatment could have been the separate oxidising melting of a large quantity of accumulated matte from various smelts, possibly with siliceous fluxes, as suggested by Agricola (Hoover and Hoover 1950: 386), but the evidence does not seem to support such a procedure (cf. chapter 7).

6.4. Experimental cupellation of archaeological samples

The aim of experimental cupellation was to determine the relative proportion of gold and silver in the solidified smelting remains, in order to assess whether this site was extracting gold as well as silver from the surrounding mineral deposits. It has been noticed that the gold-silver ratio of the ores is not modified by subjecting the minerals through the series of high-temperature processes necessary to extract the noble metals from them (Pernicka *et al.* 1998). It is therefore possible to estimate the relative proportion of gold and silver content of the ores through the analysis of cupellation products, although it will be seen that the model argued by the aforementioned authors is incorrect in a system containing matte. Significantly, these analyses will represent the actual material processed at the time, in contrast to the ore samples analysed before, which were evidently not smelted but either left behind at the mine or at the smelting site, for whichever reason. In addition, the extraction of gold and silver from the matte and the lead allows a more precise quantification of these two elements, as it avoids potential matrix effects, which might affect their quantification when other elements are present in much higher concentrations. Finally, this experimental cupellation provides a practical illustration of one of the analytical processes carried out in the laboratory of Oberstockstall, which stills shows validity today.

6.4.1. Experimental procedure

Each archaeological sample selected for cupellation was precisely weighed, put in a 32 cm-diameter bone-ash cupel of modern manufacture together with a known

weight of silver-free lead metal (Fig. 6.39), and heated at *ca.* 1250°C for around 30 minutes for the archaeological lead and between 60 and 90 minutes for the matte samples (Fig. 6.40). When a bead of precious metals was obtained at the end of the reaction, this was also carefully weighed. The experimental data are summarized below (Table 6.9). After cupellation, three silver-gold beads and three cross-sections of the used cupels were mounted in polished blocks, as explained in the methodology (cf. chapter 3), and analysed by SEM-EDS and EPMA-WDS. The remaining four beads were analysed directly and non-destructively by micro X-ray fluorescence.

Sample name	Type of sample	Sample weight (g)	Weight of added silver-free lead (g)	Cupellation outcome	Bead weight (mg)	Weight percent of noble metals in sample (%)
AN 196-01 Cup 1	Lead	19.7	11.3	Medium-size silvery bead	126.3	0.64
AN 196-01 Cup 2	Lead	20.4	14.0	Medium-size silvery bead	171.3	0.84
AN 197-01 Cup	Lead	9.4	17.4	Medium-size silvery bead	108.3	1.15
AN N01 Cup	Lead	29.8	19.9	Large silvery bead	287.3	0.96
AN 88-03 Cup	Matte	9.6	15.0	No bead, porous black crust on top (Fig. 41, right)	N/A	N/A
AN 104-01 Cup 1	Matte	10.6	33.2	Small silvery bead	15.2	0.14
AN 104-01 Cup 2	Matte	6.8	28.8	Small silvery bead	8.1	0.12
AN 108-04 Cup 1	Matte	9.7	17.1	No bead, porous black crust on top (Fig. 41, right)	N/A	N/A
AN 108-04 Cup 2	Matte	9.5	16.4	Small bead, porous black crust on top (Fig. 41, right)	6.5	0.06
AN 108-05 Cup 1	Matte	9.4	30.6	No bead	N/A	N/A
AN 108-05 Cup 2	Matte	4.8	24.6	No bead	N/A	N/A
AN 108-06 Cup 1	Matte	10.1	22.6	No bead	N/A	N/A
AN 108-06 Cup 2	Matte	7.4	31.7	No bead	N/A	N/A
AN 108-07 Cup 1	Matte	10.1	31.3	No bead	N/A	N/A
AN 108-07 Cup 2	Matte	9.0	30.1	No bead	N/A	N/A

Table 6.9. *Samples of archaeological lead and matte subjected to cupellation with the various outcomes and results from the operation.*

Fig. 6.39. *Initial set-up of the experiment: unused cupel (left) and cupel with its charge of matte (AN 108-04) and added silver-free lead (right) (photo: A. Mongiatti).*

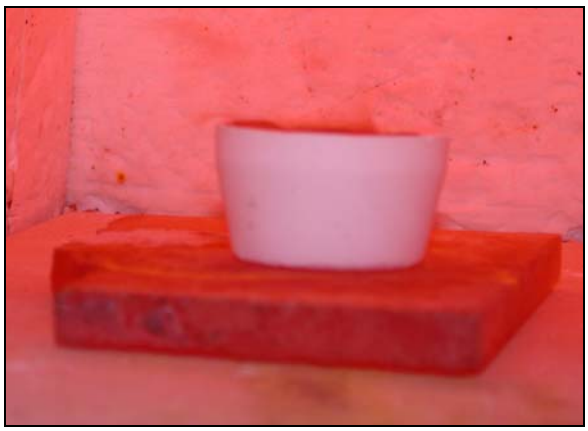


Fig. 6.40. *Heating of a loaded cupel in the electric furnace (left); hot cupel at intermediate stage with its melted charge and black iron oxide from the oxidation of the iron-rich matte on top (right) (photos: A. Mongiatti).*

The cupels used for this experiment are said to have a maximum capacity of a 30-35 gram charge, according to the manufacturer. Many samples had therefore to be split in two in order for the cupel to perform properly and not lose any of the cupelled material due to overflowing when the sample and the lead had melted together. This duplication of most experiments also allowed a counter-control of the results. These have been distinguished for each relevant sample by naming them Cup 1 and Cup 2. There were two separate sessions of cupellation, the first one including one sample of lead (AN 196-01 Cup 1 and Cup 2) and two samples of matte (AN 108-04 Cup 1 and Cup 2; AN 88-03 Cup), and the second one two samples of lead (AN 197-01 Cup and AN N01 Cup) and four samples of matte (AN 104-01 Cup 1 and Cup 2; AN 108-05 Cup 1 and Cup 2; AN 108-06 Cup 1 and Cup 2; AN 108-07 Cup 1 and Cup 2).

During the first batch of cupellations of matte samples, a black crust was observed to form at the surface of the molten charge at an early intermediate stage of the reaction, forming a type of skin on top of the charge (Fig. 6.40, right). The duration of the cupellation of matte samples was increased for the second set of samples, when it was observed that this black crust could be molten in so doing. This also explains the high working temperature, which would be unnecessary for argentiferous lead alone. To further prevent the formation of this black product, the ratio of silver-free lead/archaeological sample was also increased. The necessity for this greater weight of lead was believed to come from the presence of copper within the lead bullion. It is apparently advised to add at least twelve times the weight of the initial charge if the bullion contains silver and copper in a ratio 2-3:1, and at least sixteen times if the ratio goes down to 1:1, for the cupellation process to come to completion (Riche and Gelis 1888; Thomas *et al.* 2006). Some experimental work on the cupellation of copper-silver alloys has also shown that the ratio should be three to seventeen times the estimated weight of copper of the alloy to be cupelled (Tereygeol and Thomas 2003).This worked well for the samples of archaeological lead but not for the matte initially. For the latter, the high iron content had also to be taken into account when calculating the necessary quantity of lead, which was omitted for the first lot of cupellations and led to the formation of this iron oxide-rich black product. In the case of copper-silver alloy also containing some lead and iron, Agricola indeed recommends to add four times as much silver-free lead to the charge as if the silver was only alloyed with copper (Hoover and Hoover 1950: 250). Ercker also mentions the “sixteen times [the weight of the charge for] the amount of lead” or “sixteen centners or units” when assaying matte and crude copper respectively, but in some cases actually add the lead at the scorification stage prior to cupellation and only cupel the clean and smaller lead bullion (Sisco and Smith 1951: 47, 51-53). Specimens of this black crust were mounted in polished blocks similarly as before and analysed by SEM-EDS to determine their nature and verify that they did not retain too much silver.

Another aspect of this experiment was to try to better understand the practical side of cupellation and which parameters could influence it, and most importantly how feasible and effective the cupellation of matte could be. Various ratios of silver-free lead/archaeological sample were prepared to see if some combinations would fail or modify the process or the results. Large and small charges were tested for

each sample to investigate the physical limitations of the cupels. These were however not reached since all cupellations appear to have taken place correctly until the end, except for the formation of the black product when cupelling matte, which was independent of the reaction vessels. Modifying the lead/matte ratio was also performed in order to see if a threshold had to be reached before achieving complete separation and make sure no precious metals were lost in the operation. It has however not been possible to bring a definite answer to this side of the study, as longer process duration appeared to solve the problem, independently of the charge or silver-free lead/matte ratio.

6.4.2. Results

The cupellation reactions led to a variety of outcomes, from the production of relatively large silver-gold beads to virtually nothing except for the used cupel soaked in lead oxide and other base metal oxides, and to the black porous crust mentioned above in the case of some matte samples. The results of the experiments and the weights of the beads, when obtained, are presented in Table 6.9 above. Analytical data of the analysed beads, cupel sections and black crust specimens are presented in the following tables (Table 6.10 and 6.11). Characteristic pictures have also been selected for each type of material to illustrate the results of this experiment.

6.4.2.1. Silver-gold beads

All the archaeological lead samples produced a bead, of relatively medium to large sizes (Fig. 6.41). Their weight is on average slightly lower than 1 % of the original sample, with values ranging from 0.6 to 1.2 %. On the other hand, the beads produced by the cupellation of matte are only 0.1 % of the weight of the cupelled sample. There is therefore about ten times less noble metals in the matte phase than in the lead bullion, or in other words, the matte has *ca.* 10% of the noble metal content of the bullion.

The beads from the two cupellations of archaeological lead AN 196-01 (AN 196-01 Cup 1/S1 and AN 196-01 Cup 2) were mounted as polished blocks and analysed by SEM-EDS and EPMA-WDS, while the others were all analysed without preparation by micro XRF. Similarly for the matte samples, only the bead from the

first batch of cupellations (AN 108-04 Cup 2) was prepared as an epoxy resin block and analysed in the SEM (Fig. 6.42), while the other two beads produced by the cupellation of matte AN 108-04 were analysed by micro XRF. Their chemical composition are presented in Tables 6.10 and 6.11.

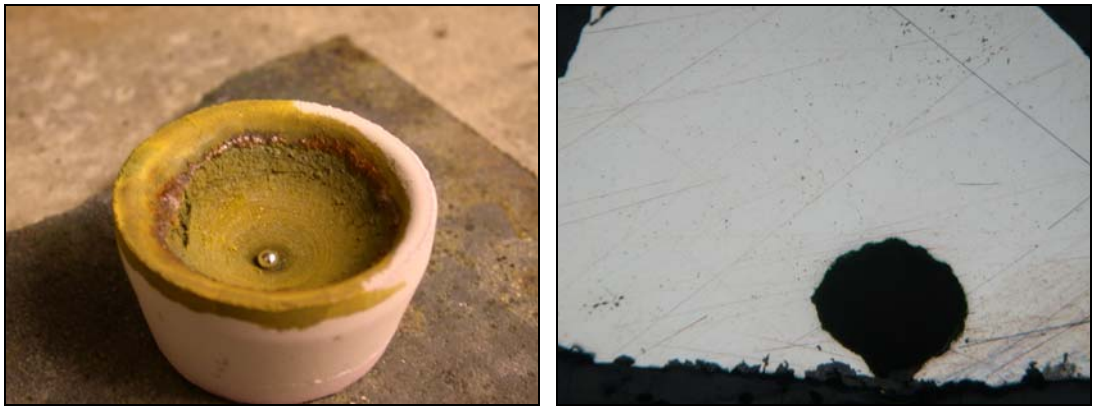


Fig. 6.41. *Left: silver-gold bead from the cupellation of an archaeological lead sample (AN 196-01 Cup 2), the yellow-green colouration of the cupel is due to the absorption of lead oxide and a mixture of other base metal oxides (photo: A. Mongiatti). Right: cross-section of the same bead under the optical microscope. Note the pore at its base and the darker areas on the bottom line where the bead was attached to the cupel (AN 196-01 Cup 1/S1, optical microscope, plane polarised light, 50x, long axis ~2 mm).*

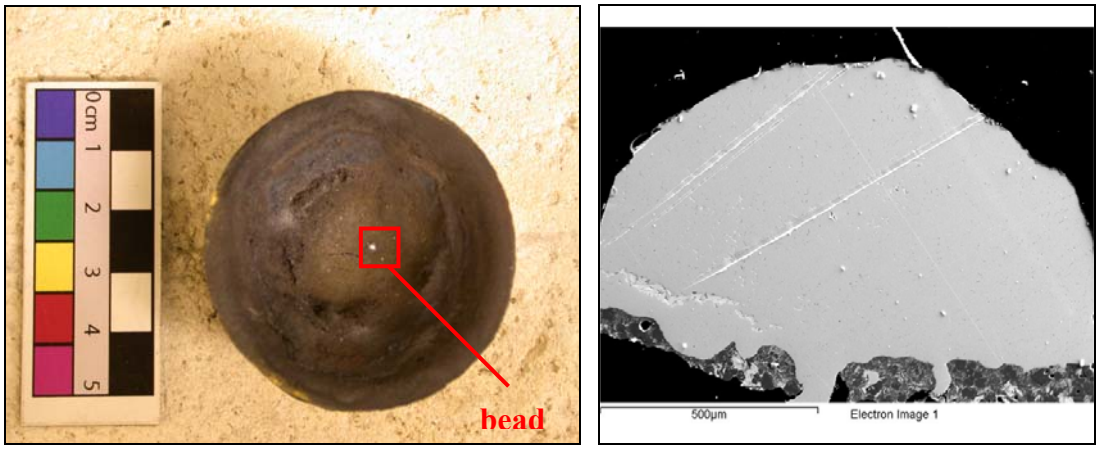


Fig. 6.42. *Left: silver-gold bead from the cupellation of an archaeological matte sample (AN 108-04 Cup 2), note the black colouration of the cupel different from the lead sample one. This black colour is most likely due to the relatively high proportion of iron oxide in the mixture of oxidised base metals (photo: A. Mongiatti). Right: backscattered image of the same bead with the residual dark bottom areas of adhering cupellation material soaked with lead oxide (AN 108-04 Cup 2/S1, BSE, 100x).*

The gold content ranges from 22 to 25 wt% in three of the four beads obtained from cupelled lead, with one sample showing only 6 wt% (AN 197-01 Cup), while it varies between 0.2 and 3 wt% in the three beads obtained from matte samples. Areas close to the top surface of the beads, i.e. where cupellation has been brought nearer to completion, contain up to 0.4 wt% of copper, 0.4 wt% of bismuth and 8.6 wt% of lead (Table 6.10). The comparison between the top and bottom surfaces of several beads analysed by micro XRF has not surprisingly shown a much higher concentration of lead at the bottom (6-12 wt% Pb, 14 wt% average), where it was less easily oxidised, or possibly present in the form of lead oxide in particles of cupels still adhered to the bead (Tables 6.10-6.11). These areas also show higher levels of base metal impurities, the bead from the furnace bottom showing particularly high bismuth content (10 wt% Bi). This range of concentration in bismuth especially at the interface bead/cupel is very similar to that from Oberstockstall (Rehren 1998), showing that all the bismuth initially present in the ore would preferentially go into the bullion and be removed together with lead through cupellation. These traces of lead, copper, and bismuth detected in most samples simply show our relative lack of skill at performing cupellation, but this did not interfere with the calculation of the gold/silver ratios of the beads. To some extent, the loss in silver-gold prills within the cupels has not prevented this estimation of the composition of the silver-gold alloys produced either.

	Type of sample	Ag wt%	Au wt%	Pb wt%	Cu wt%	Bi wt%
AN 196-01 Cup 1/S1[(1)]	Lead	76.4	22.8	0.7	b.d.l.	0.1
AN 196-01 Cup 2[(1)]	Lead	74.3	24.9	0.6	0.1	0.1
AN 197-01 Cup/S1[(2)]	Lead	93.5	5.9	0.5	b.d.l.	0.1
AN N01 Cup/S1[(2)]	Lead	77.3	22.1	0.1	0.1	0.4
AN 104-01 Cup 1/S1[(2)]	Matte	88.6	2.2	8.6	0.3	0.3
AN 104-01 Cup 2/S1[(2)]	Matte	97.0	2.9	0.1	b.d.l.	0.0
AN 108-04 Cup 2/S1[(1)]	Matte	98.2	0.2	1.2	0.4	b.d.l.

Table 6.10. *Chemical composition of the silver-gold beads produced by cupellation. Analytical data obtained by SEM-EDS[(1)] as well as micro XRF[(2)]. The data from the micro XRF analyses were obtained on the top surface of the beads (normalised to 100 wt%, b.d.l.: below detection limit).*

	Type of sample	Ag wt%	Au wt%	Pb wt%	Cu wt%	Bi wt%
AN 197-01 Cup/S1	Lead	89.4	4.8	5.2	0.0	0.6
AN N01 Cup/S1	Lead	63.6	12.0	14.1	0.8	9.7
AN 104-01 Cup 1/S1	Matte	77.1	1.7	19.7	0.5	1.0
AN 104-01 Cup 2/S1	Matte	81.4	2.2	15.3	0.3	0.8

Table 6.11. *Micro XRF data from the bottom sides of the beads showing overall a higher lead content (data normalised to 100 wt%, b.d.l.: below detection limit).*

There appears to be significantly more gold in the silver collected in the lead bullion within the smelting furnace than lost with the silver trapped in matte. This may be explained by the fact that gold has a much higher density (*ca.* 19) than the other elements (*ca.* 10 for silver, *ca.* 11 for lead and *ca.* 2 for sulphur), and that silver has a higher chemical reactivity than gold. The latter is inert and therefore remains in the metallic state, while silver has a greater affinity with sulphur and therefore can be more easily chemically bound in matte.

The gold/silver ratio is on average 0.27 for the three beads from archaeological lead of similar composition, and 0.06 for the low-gold content bead. This same ratio is down to 0.03 in two beads produced by the cupellation of one cupelled matte sample, with the third bead showing a very low ratio of 0.001 for a second matte sample. These data would suggest that in the ores processed at the Angertal site, for each quantity of silver produced over one fourth was gold on average, except for one sample, which appears poorer in gold than the others and closer to the concentrations of beads from matte sample AN 104-01 (Table 6.1, p. 204). The little quantity of gold recovered from the matte samples was most likely originally in prills of lead bullion, which did not diffuse totally and remained trapped in the matte layer. These values, despite showing a dramatic discrepancy for one sample, certainly indicate that the ores from the neighbouring mines were exploited for their gold content, with silver also being a valuable product of this industry.

6.4.2.2. Cross-sections of used cupels

Three cupels from these experiments were sectioned and mounted as thick blocks of epoxy resin similarly to archaeological samples (Fig. 6.43). These cross-sections were analysed from top to bottom to identify the composition of the absorbed

mixture of base metal oxides and estimate the gradient of absorption of this lead oxide-rich mixture.

As seen on earlier pictures, the cupels used for the cupellation of archaeological lead put on a yellow-green colour from the absorption of lead oxide, while they became a deep black-brownish colour upon the cupellation of matte, most likely because the mixture of oxidising metals was a lot richer in iron oxide (Fig. 6.41-43). These cupel sections were analysed by SEM-EDS; bulk analyses were obtained at magnification 100x starting close to the upper surface of the cupel and going further down. Most analytical totals of area analyses did not add up to 100 wt% when not normalised (70-95 wt%, 87 wt% average), because of the remaining porosity in the vessels showing that only part of the pores has been filled with lead oxide.

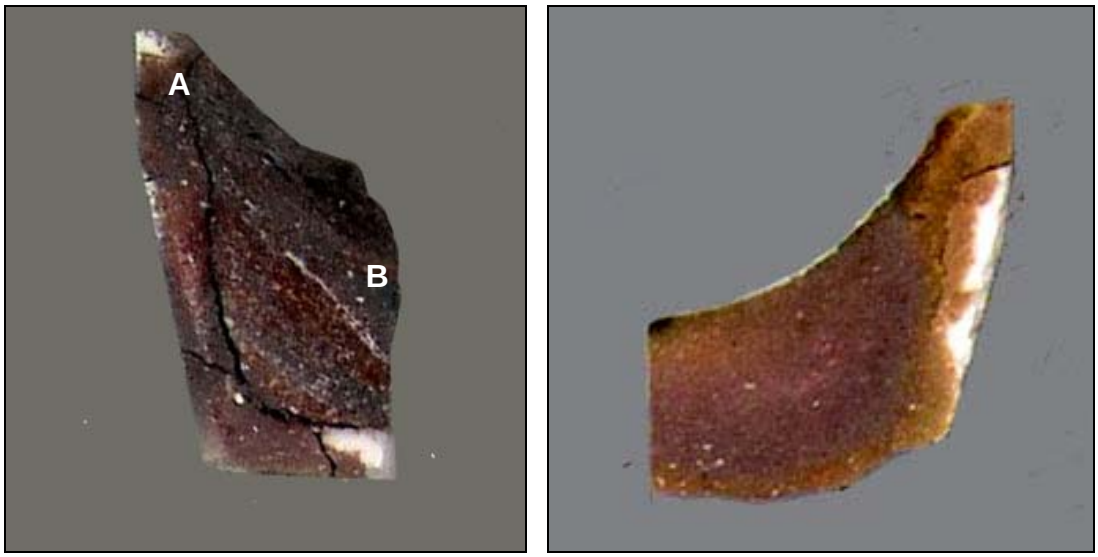


Fig. 6.43. *Cross-sections of cupels after use for the cupellation of archaeological matte (left, AN 108-04 Cup 2/S2) and lead (right, AN 196 Cup1/S2) samples (scan of resin blocks, long axis ~3 cm).*

The bulk of the cupel used for the cupellation of archaeological lead sample AN 196-01 was mainly composed of calcium oxide, phosphorus oxide, lead oxide, with minor amounts of silica, magnesia, soda and arsenic oxide (Table 6.12, AN 196-01 Cup1/S2). Calcium oxide and phosphorus oxide are part of the original structure of the cupel in the form of hydroxylapatite ($Ca_5(PO_4)_3(OH)$); these are combined with small quantities of silica, magnesia and some soda (Fig. 6.44). Lead oxide on the other hand has been absorbed by the porous cupel upon use. Antimony oxide was detected in areas close the top of the cupel (up to 2 wt% Sb_2O_3), while arsenic oxide

was identified towards the bottom of the cupel (up to 4 wt% As_2O_3). Gradient and variation in the oxidation and therefore absorption of the various base metals contained in the initial lead bullion is a rather expected pattern because of the differences between their oxidation potentials. Arsenic tends to oxidise very easily, it would therefore be part of the first base metals to be eliminated from the bullion and absorbed into the cupel; most of the arsenic oxide would, however, vaporise due to its high volatility. Copper oxide was detected locally in concentrations around 1 wt% CuO, also close to the bottom of the cupel, suggesting that it was also among the earliest base metals to oxidise. No iron oxide has been identified in this sample; this is a clear difference to cupels used for matte cupellation as shown below.

	Na_2O wt%	MgO wt%	SiO_2 wt%	P_2O_5 wt%	SO_3 wt%	CaO wt%	FeO wt%	CuO wt%	As_2O_3	PbO wt%
AN 196-01 Cup 1/S2	1.1	0.8	1.8	31.7	b.d.l.	39.5	b.d.l.	b.d.l.	0.6	24.5
AN 108-04 Cup 2/S2	1.6	0.8	1.4	31.0	4.6	38.6	4.0	1.4	b.d.l.	16.6
AN 88-03 Cup/S1	1.5	0.9	1.1	34.2	5.8	41.1	3.2	1.2	b.d.l.	11.0

Table 6.12. *Averages of bulk compositions of used cupels obtained by SEM-EDS (data normalised to 100 wt%, b.d.l.: below detection limit), and calculated out of 4, 12 and 9 area analyses at magnification 100x for AN 196-01 Cup1/S2, AN 108-04 Cup 2/S2 and AN 88-03 Cup/S1 respectively. See appendix 5 for the full results.*

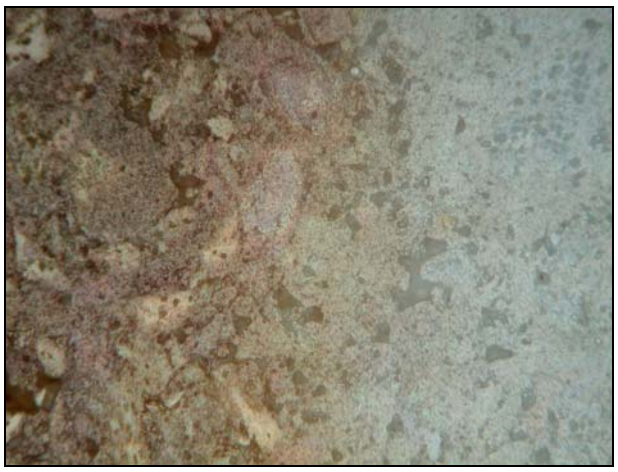


Fig. 6.44. *Microstructure of a used cupel after the cupellation of an archaeological sample of lead. The right side is the original structure of the cupel while the left side shows the absorption of base metal oxides (AN 196-01 Cup1/S2, optical microscope, plane polarised light, 100x, long axis ~1 mm).*

The two sections of the cupels used for the cupellation of matte (AN 108-04 Cup 2 and AN 88-03) display similar microstructures and chemical compositions (Fig. 6.45); hydroxylapatite crystals having partially reacted with the lead-oxide rich mixture can clearly be seen (Fig. 6.46). Bulk analyses of specimen AN 108-04 Cup 2/S2 show high levels of calcium oxide (30-47 wt% CaO) and phosphorus oxide (25-37 wt% P_2O_5) (Table 6.12). Lead oxide varies from 4 wt% PbO close to the top

surface and the outer rim of the cupel (area A, Fig. 6.43) to 28 wt% PbO close to the bottom and the surface of the central depression (area B, Fig. 6.43), with an average of *ca.* 17 wt% overall in the body of the soaked cupel. Iron oxide ranges from below detectable levels up to 17 wt% FeO, moving from the outer rim to the centre of the cupel, with an average of *ca.* 4 wt%. Copper oxide varies below detectable concentrations to 3 wt% CuO. Iron and copper oxides also showed local concentrations of 30-32 wt% FeO and 7-9 wt% CuO respectively, in phases of lead oxide, which have run and solidified into the pores of the cupel. The oxidised sulphur originally contained in the matte has partially vaporised and partially been absorbed in the cupel matrix, which showed levels between 2 and 9 wt% SO_3 in areas where it has been detected, with an average of 4 wt%; areas close to the central depression appear devoid of it at detectable levels. Silica and magnesia are in concentrations of the same levels as in the previous cupel, i.e. *ca.* 1 wt% for each. No antimony or arsenic oxides were detected in this specimen.

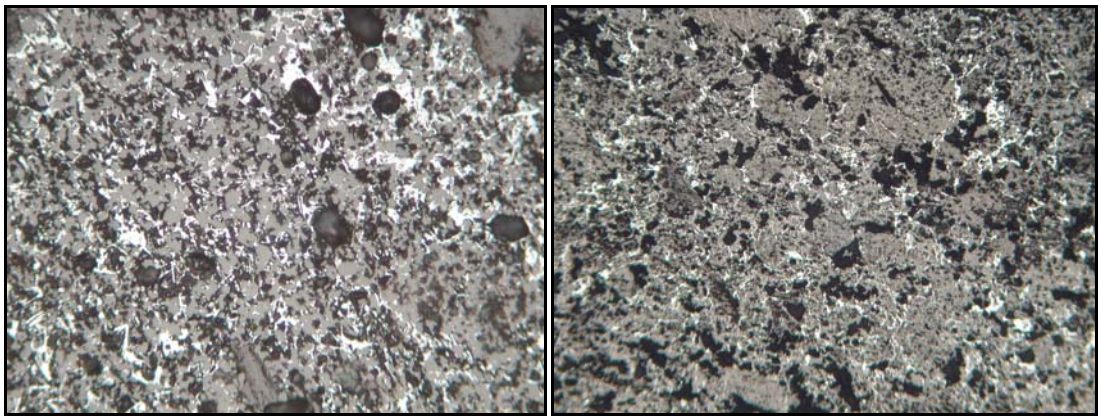


Fig. 6.45. *Microstructures of used cupels after the cupellation of archaeological samples of matte. Note the porosity partially filled with bright iron oxide-rich phases of lead oxide (left: AN 108-04 Cup2/S2; right: AN 88-03 Cup/S1, optical microscope, plane polarised light, 100x, long axis ~1 mm).*

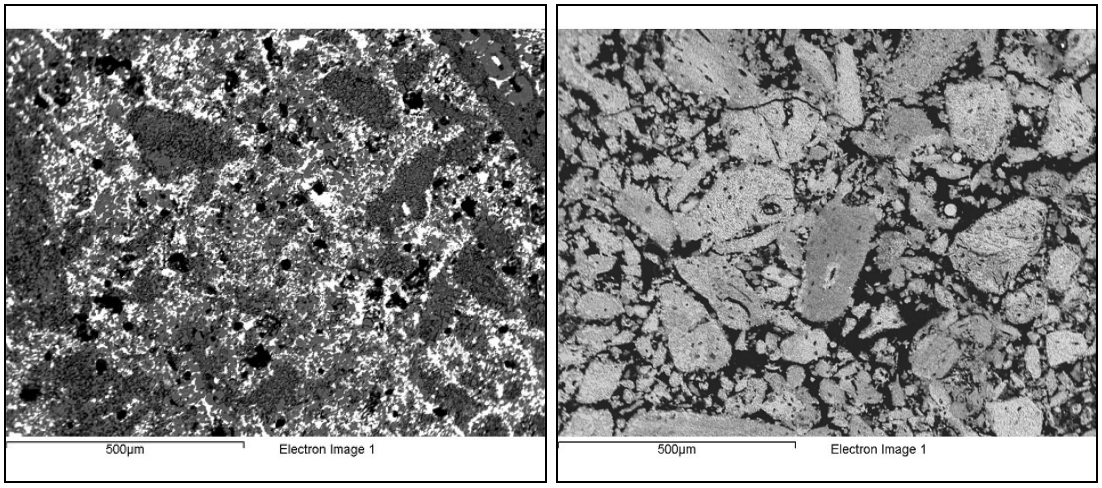


Fig. 6.46. *Microstructures of the used cupels of Fig. 6.45: note the numerous apatite particles, which have been partially absorbed by the surrounding molten mixture of base metal oxides, especially on the left image (left: AN 108-04 Cup2/S2; right: AN 88-03 Cup/S1, BSE, 100x).*

The analysis of the specimen AN 88-03 Cup/S2 revealed a very similar composition with calcium oxide (34-49 wt% CaO), phosphorus oxide (27-41 wt% P_2O_5), lead oxide (4-17 wt% PbO), sulphur oxide (1 to 10 wt% SO_3), iron oxide (2-13 wt% FeO), and copper oxide (1-6 wt% CuO) (Table 6.12). The outer and bottom areas of the cupel do not seem as soaked with base metal oxides as the central part where the depression lays, which contains the oxidising melted charge. In several of these areas, only sulphur oxide can be detected in low amounts (1 to 4 wt% SO_3) as a contaminant to the original cupel matrix. The cupellation of this matte sample did not lead to the formation of a silver-gold bead on the surface of the depression. It seems however that there were some precious metals in this sample as shown by a noticeable drop stuck to the bottom of the cupel (Fig. 6.47). This suggests that the operation may not have been performed properly since the noble metals were not recovered in the right way. The analysis of this drop revealed a silver-gold alloy with 90 wt% silver and 10 wt% gold. This appears to be a much higher relative concentration of gold than shown by the analyses of the other beads resulting from the cupellation of matte. This could be explained by either the fact that this matte may have been produced by a specific smelting operation during which a lot more gold was lost in the matte, or more likely that a silver-gold bead was left on the ceramic plate on which the cupels are placed during cupellation (Fig. 6.41) from a poor previous cupellation, and therefore melted upon re-heating and got stuck to the bottom of this cupel.

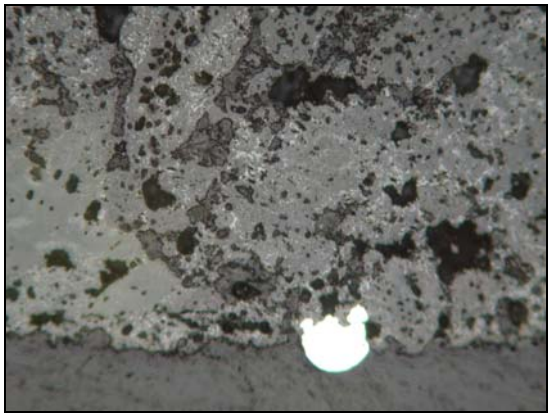


Fig. 6.47. *Gold-rich silver bead attached to the bottom of the cupel (AN 88-03 Cup/S1, optical microscope, plane polarised light, 100x, long axis ~1 mm).*

In both cupels used for the cupellation of matte, numerous separate phases of copper metal containing 1 to 2 wt% of iron can clearly be seen in various areas of the body of the vessel (Fig. 6.48). The copper still in metallic phase indicates that there was not enough lead to recover the silver from it (Bayley and Eckstein 1997) and trigger its oxidation in addition to that of iron. These copper phases could have failed the quantitative assessment of the operation by dissolving some silver in them. However in our case, the presence of metallic copper does not seem to have interfered with the cupellation process since no silver has been detected in these numerous copper prills.

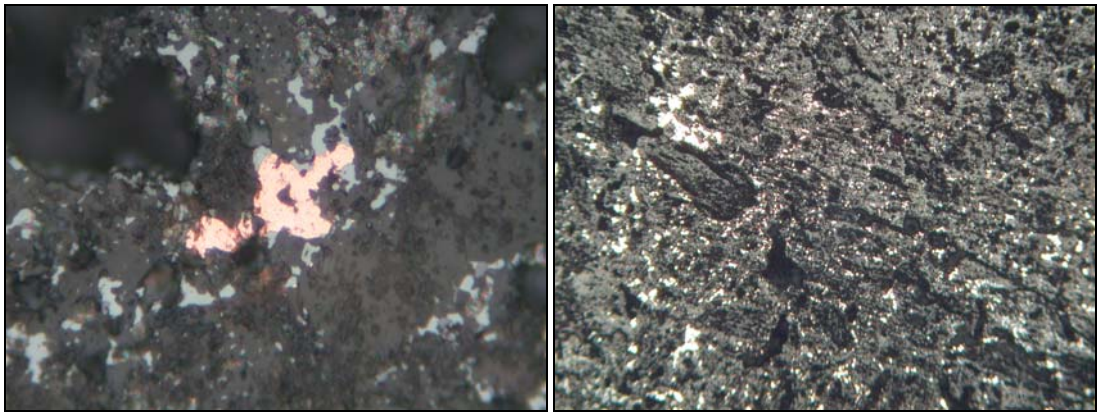


Fig.6.48. *Bright separate phases of metallic copper within the body of cupels (optical microscope, plane polarised light, left: AN 108-04 Cup 2/S2, 500x, long axis ~200 µm; right: AN 88-03 Cup/S1, 100x, long axis ~1 mm).*

6.4.2.3. Black surface crust

For the initial group of cupellation of matte samples, a black crust was observed forming on the surface of the molten charge for the suspected reasons explained

above. Attempts were made to avoid its formation the second time cupellation was performed, and when this undesired product formed, it was observed that increasing the duration of the operation could eliminate it.

The crust from two cupellations, which did not lead to the formation of beads of precious metals, was mounted as polished blocks in order to identify its composition and try to determine the reason of its formation. Both products from the cupellation of matte AN 108-04 and AN 88-03 showed similar microstructure and chemical composition, with a variety of numerous iron oxide-rich crystals in a lead oxide matrix rich in other base metal oxides such as copper, iron and zinc (Fig. 6.49). Area analyses by SEM-EDS show that sample AN 108-04 Cup 1 is mostly composed of iron oxide (43-64 wt% FeO) and lead oxide (30-51 wt% PbO), with minor amounts of copper oxide (5 wt% CuO) and zinc oxide (2 wt% ZnO), while AN 88-03 Cup/S2 contains more iron oxide (68-79 wt% FeO) and less lead oxide (21-29 wt% PbO), with some copper oxide (2-3 wt% CuO).

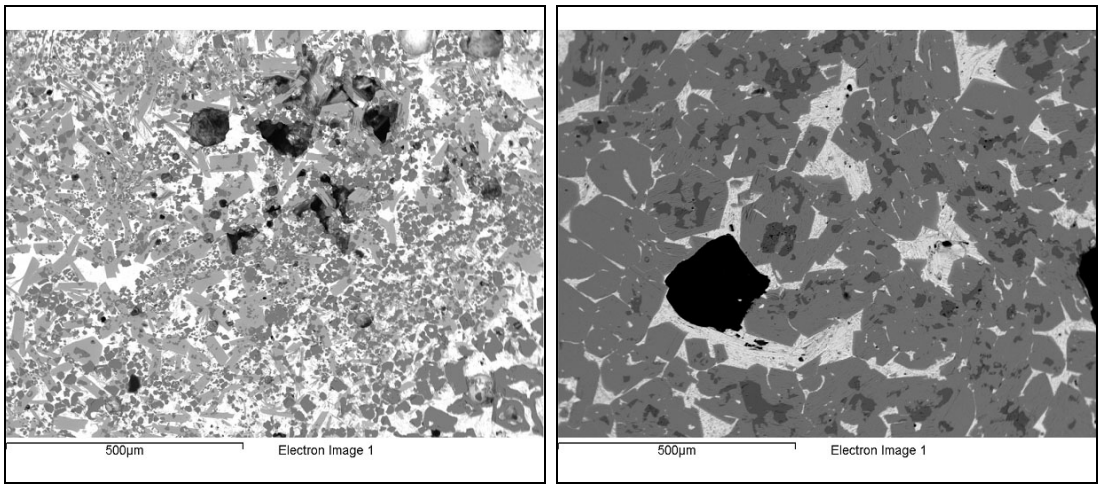


Fig. 6.49. *Microstructure of the black crust resulting from the cupellation of matte samples. Note the difference in size between the dark grey crystals of magnetite and the overall proportion between lead oxide (bright phase) and iron oxide (dark grey crystals) (BSE, 100x, left: AN 108-04 Cup 1, right: AN 88-03 Cup/S2).*

The black crust from AN 108-04 Cup 1 more precisely displays many large acicular crystals rich in iron oxide and lead oxide (72 wt% FeO, 28 wt% PbO) and numerous relatively smaller phases of magnetite; both types of crystals are highly indicative of the strongly oxidising conditions of the reaction. This sample also shows large areas of metal, which are rich in lead (65 wt% Pb), silicon (15 wt% Si), copper (11 wt% Cu), iron (1 wt% Fe), and oxygen (8 wt% O), the oxygen being

most likely associated to silicon as silica crystals originating from the polishing process and the rest indicating slight oxidation of the metallic phase (Fig. 6.50). AN 88-03 Cup/S2 exhibits a very similar microstructure with a mixture of the iron oxide- and lead oxide-rich phases described above and magnetite crystals, but with a crystal growth more evenly distributed in all directions for the former and a higher density of crystals generally rich in iron oxide compared to the lead oxide-rich phase, generally reflecting dissimilarities in the experimental conditions of the reaction (Fig. 6.51). A few prills have been identified in both samples, a copper prill containing 2 wt% of silver in AN 108-04 Cup 1/S2 and a gold-silver bead (96 wt% Au, 4 wt% Ag) in AN 88-03 Cup/S2. This loss in precious metals in this iron oxide- and lead oxide-rich product may explain the absence of bead at the end of the cupellation: most probably a small amount of gold and silver remained trapped in this crust. It was possible to avoid this loss in later cupellation experiments by increasing the duration of the reaction and thus allowing the elimination of this crust.

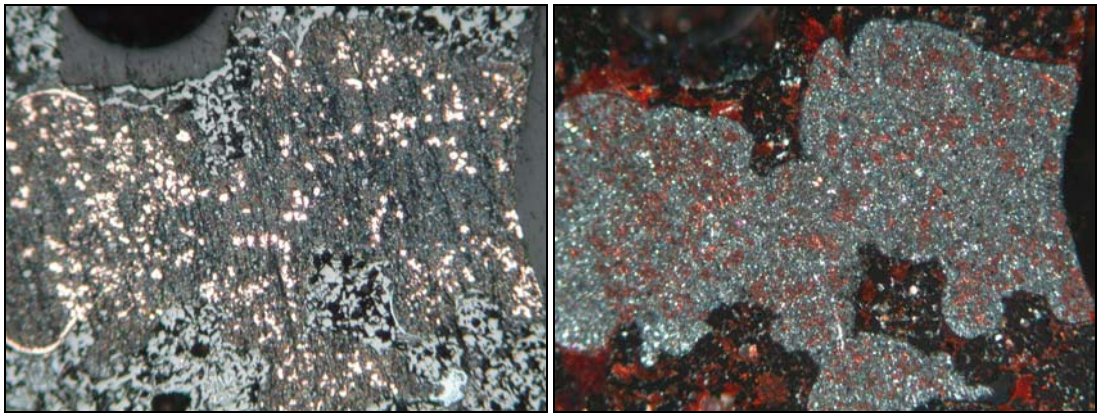


Fig. 6.50. *Large metallic phase composed of a lead matrix including numerous small crystals of silicon carbide from the polishing process, and bright prills of copper (AN 108-04 Cup 1, optical microscope, plane (left) and crossed (right) polarised light, 100x, long axis ~1 mm).*

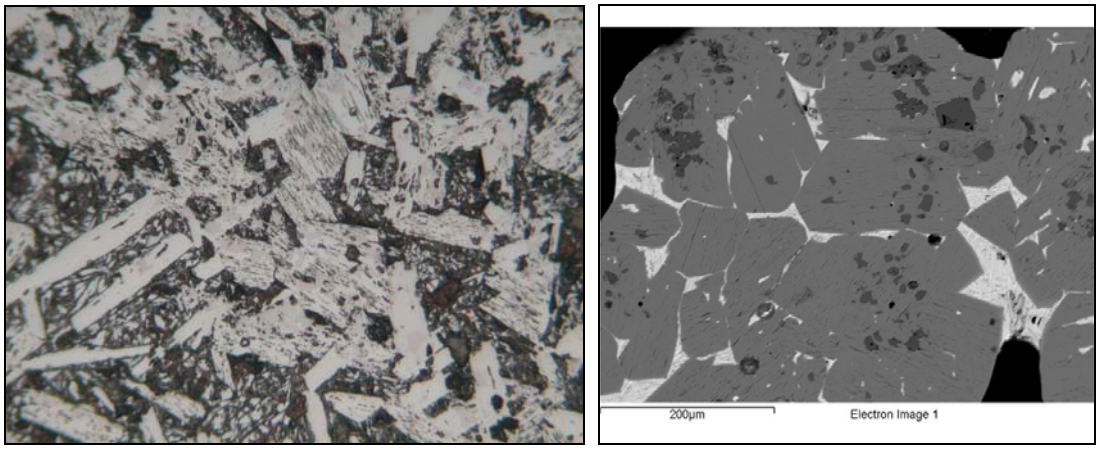


Fig. 6.51. *Variation in the growth of crystals rich in iron oxide- and lead oxide: acicular crystals for AN 108-04 Cup1 (left: optical microscope, plane polarised light, 200x, long axis ~500 µm) and large crystals grown in every direction for AN 88-03 Cup/S2 (right, BSE, 200x).*

6.5. Reconstruction of the smelting process

The analytical results obtained on the various archaeological materials contribute towards a relatively comprehensive image of the extractive technology of gold and silver at the Angertal smelting site. It seems clear that the smelting process used locally extracted sulphidic ores and produced three main phases: lead-rich bullion, matte, and slag. These phases are immiscible and have different densities; however, the small metal globules found within slag and matte, and the sulphidic inclusions within the slag, both due to incomplete mechanical separation, suggest that all three formed in a single smelting step and were in close contact. Therefore it can be assumed that they formed three different layers within a single furnace. This is confirmed by the large piece found at the bottom of one of the three furnaces, whose section shows this characteristic sequence of metallic lead, matte and slag distributed from bottom to top. The bottom layer, largely dominated by lead metal, collected the noble metals and was further processed by cupellation – hence its absence from the archaeological record. Matte and slag were tapped out of the furnace, possibly in forehearths similar to those depicted in contemporary texts in front of the furnaces (Fig. 6.52), where they solidified as distinct layers. Slag was then most certainly discarded and matte probably as well, because of their likely insignificant content in precious metals. In the case of matte, however, the situation may be different if this waste product was considered to hold non-negligible quantities of noble metals to be recovered and could have instead potentially been recycled in subsequent smelting

operations or separately re-melted with additives. This issue among other topics will be discussed in more detail in the next chapter (cf. chapter 7) and is introduced below when interpreting the results from the analyses of each type of material, i.e. ore, slag, matte and ceramic, described in the previous section of this chapter.

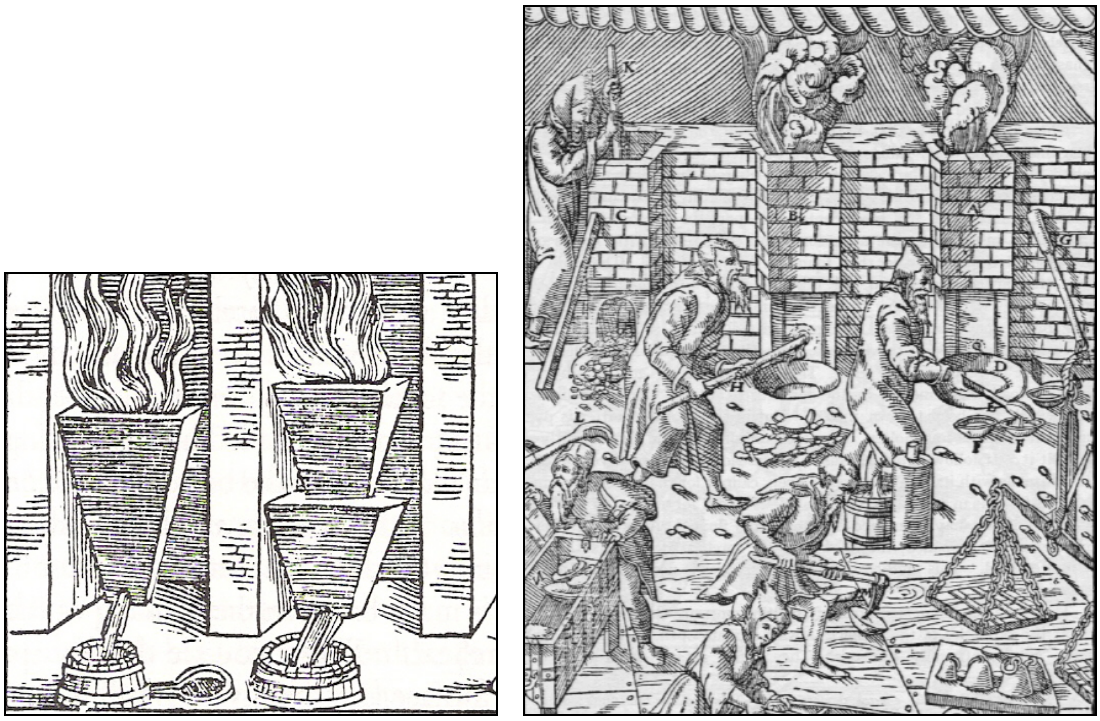


Fig. 6.52. *Sixteenth-century depictions of smelting furnaces: the furnaces of Biringuccio (left, after Smith and Gnudi 1990: 150), used for any kind of ore, and one type of furnace for gold ores by Agricola (right, after Hoover and Hoover 1950: 383). Note the representation of forehearths in both drawings, the channels linking the furnaces and the forehearths in the drawing on the left, and the use of hooked bars by the smelters in the illustration on the right.*

6.5.1. The types of ore processed

The analytical data from the ore selected from the mining sites of the Bockhart and the Erzwies show a variety of sulphidic ores, which could have been processed at the closely located Angertal smelting site, such as galena, pyrite and sphalerite, as well as chalcopyrite and arsenopyrite, and most likely some fahlore. The small number of analysed fragments does not allow an accurate estimation of the relative proportions of each ore at the time of intense exploitation in the sixteenth century, but it would seem that the lead-, iron- and zinc-rich minerals are in larger quantity than the copper- and arsenic-rich ones within the small sample of ores considered. The broadly similar dimensions of all selected fragments of ores indicate that they

were probably sorted and crushed to standard size, for instance at the ore dressing plant located close to the Bockhart mine, before being brought to the smelting site down in the valley. This would allow an efficient sorting of the ore and would additionally save on the weight to be transported down if the gangue was partially removed beforehand, still bearing in mind that in the case of the process carried out at the Angertal, part of the gangue would still need to be kept in order for the ore mixture to be self-fluxing.

The presence of lead, copper, iron and zinc sulphides, and of silver, antimony and arsenic within prills and sulphidic phases in the slag and matte samples analysed, indicates that similar base-metal sulphidic ores and more complex silver- and gold-bearing fahlores containing iron, antimony, copper, lead and arsenic were smelted at the excavated site in the Angertal. The analytical determination of the different elements in smelting waste products, which led to the identification of these various ores at the smelting site, further links the smelting site of the Angertal to the surrounding mines of the Bockhart and the Erzwies located higher up in the mountains, which is in good agreement with historical texts . The overall lower levels of arsenic in the various metallurgical products from the smelting do not seem to support the hypothesis that the main ore smelted at this site in the sixteenth century was arsenopyrite or predominantly rich in arsenopyrite. The definite presence of pieces of arsenopyrite ore at the smelting site, although from disturbed layers, and the existence of gold-rich arsenopyrite-quartz veins are, however, documented archaeologically and geologically, as well as in written sources (Cech and Walach 2001: 298; Cech 2007: 7) and clearly point out that arsenopyritic ores were exploited at one time for their gold content. These could have been smelted nearby, but smelting site H1 may not have been the location where this particular type of ore was processed at the period studied as no evidence has been found to substantiate this hypothesis. As mentioned before, another explanation could be this specific focusing of the miners on minerals particularly rich in precious metals, amongst which arsenopyrite may have not been included, and it is possible that all these rich sulphides were embedded in the main arsenopyrite vein, but extracted selectively. Such a scenario would repeat the observation documented for the Oberharz at the same period (Bartels 1992).

This apparent absence of arsenopyrite may otherwise be explained by a division of specific tasks between the various smelting sites in the valley. The separation may

have been between the two relevant metals, gold and silver, some smelting sites extracting silver-containing gold and others gold-rich silver. This could have led to the smelting of specific ores at each site, site H1 hence not dealing with arsenopyrite. Another explanation could have been that each smelting site had its ore supply arriving from distinct mines or veins, again naturally associated to one noble metal more than the other. This type of organisation per mine could find justification in economic and ownership reasons, and an incentive in the fact that it could avoid the need to assay every ore charge. It may therefore have been relevant to keep different types of ore mixtures separate. This question is extremely difficult to answer in light of the present data because of the wide range of minerals found at all three sites. The distinctive behaviour of the elements identified in the analysed metallurgical products at high temperature further complicates the matter as it results in a discrepancy between elemental concentrations: some elements such as arsenic and zinc partially vaporise during the smelting and are lost; the detected quantities do not therefore reflect their original concentrations in the raw materials.

The selected ore fragments from the Bockhart mine could date to the final phase of mining, and be an indication of the impoverishment of the veins in gold and silver towards the end of the sixteenth century, hence the absence of gold in detectable levels (<10 ppm). This decrease in valuable quantities of noble metals in the ore, especially gold, could have explained why the smelting site of the Angertal was abandoned, another potential reason being the running out of fuel due to intense deforestation and the consequent delocalisation of the smelting operation to another area (Cech and Walach 1999). Besides, the pieces of ore found at the Angertal site were recovered from disturbed levels and may belong to a contemporary or later phase of exploitation, hence perhaps reflecting the contemporaneous or earlier impoverishment of the ores in noble metals in the neighbouring mining exploitations. There is thus a slight uncertainty regarding the exact nature and content in noble metals of the ores processed in the Angertal valley in the sixteenth century, but it appears from historical sources and from the present data (cf. 6.5.4 below) that they contained relatively high quantities of precious metals. Although it does not inform directly about the grade of the ore, the gold/silver ratio identified by cupellation in the lead bullion gives the relative proportion of gold found in this bullion, and seems to reliably suggest that the ores smelted in the sixteenth century in the Angertal were fairly rich. Another factor to consider here is that the minerals

found in the archaeological assemblage are also precisely the one, which were discarded and left behind perhaps because they were rich in waste material and poor in metal-rich minerals; they may therefore never be fully representative of the minerals actually smelted, or only inform about the type of ores processed but not about their richness.

6.5.2. Typical fayalitic smelting slag

As seen in the characterisation section, the slag has a typical fayalitic structure, documented in many other smelting operations. In the case of the Angertal, this slag also includes numerous inclusions of matte and several lead prills, which did not separate from the low-viscosity slag. The temperature of formation of fayalite crystals ranges between *ca.* 1150 and 1200 °C, and as seen on the diagram below, all slag samples analysed for their bulk composition gather together in this temperature region (Fig. 6.53). The high concentrations of alkali oxides may further suggest that the liquidus temperature of the slag has probably even been slightly lower; they would have also helped the ore mixture to become self-fluxing. This gives us an estimation of the minimum temperature achieved in the furnace. The amount of lime detected in most specimens further corroborates this estimation of the working temperature of the furnace, as it can be seen that calcium oxide concentrations also are drawn in the same temperature range (Fig. 6.54). On both diagrams, several samples plotting at one extreme and showing higher concentrations of silica seem to suggest that temperatures between 1300 and 1400 °C may have also occasionally been reached while smelting.

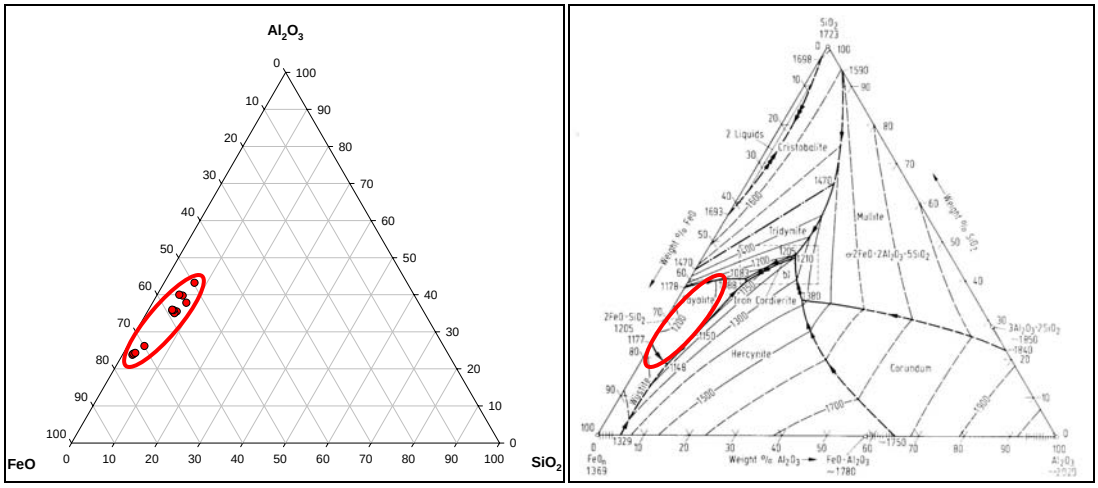


Fig. 6.53. *Diagrams plotting the distribution of slag samples in the ternary system Al_2O_3-SiO_2-FeO, showing the correlation between the range of concentration of the three oxides (left) and the temperature zone of formation of fayalite. Note the samples with a higher silica content suggesting that higher temperatures were also possibly occasionally achieved (right, after Allibert* et al. *1995: 111).*

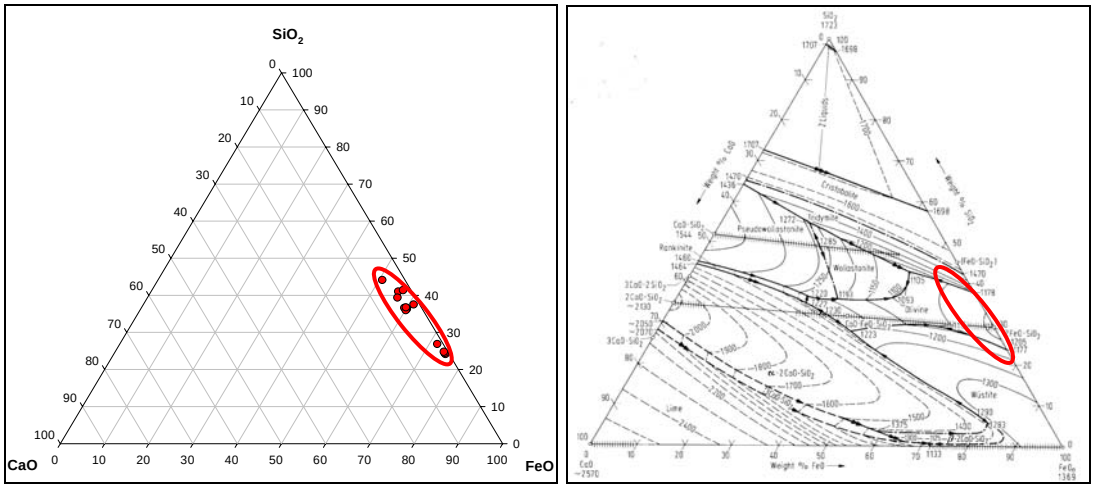


Fig. 6.54. *Diagrams plotting the distribution of slag samples in the ternary system FeO-SiO_2-CaO, further correlating the temperature range of fayalitic slag (right, after Allibert* et al. *1995: 126) with the concentration in lime. Similarly to Fig. 6.53, note the samples with a higher silica content suggesting the potential higher furnace temperatures.*

Slag principally formed from the reaction between the oxidising iron sulphides contained in the ore mixtures or the iron carbonate-rich gangue and the silica, also part of the gangue of the ores. Various oxides such as lime, potash and magnesia are probably a contribution of the charcoal to the slag (Fig. 6.55), with potash also partially coming from the furnace wall material, being formerly possibly included in feldspar. Others such as alumina or titanium oxide were most likely a contribution

from the melted ceramic of the furnace wall, while manganese oxide was introduced in the slag by the gangue. The relatively wide range of levels of manganese oxide detected in slag samples when compared to the other components may reflect a variation in the overall quantity of manganese oxide-rich iron carbonate gangue included in the ores to be smelted (Fig. 6.56). The spot analyses of several of these iron carbonate phases gave a FeO/MnO ratio which varies between 2 and 5 with an average of 3, while this ratio increases in the slag to between 5 and 22 with an average of 11, showing that this enrichment in iron oxide is not only a contribution from the gangue. This further indicates that the proportion of iron coming from the gangue could vary greatly, the remaining quantity of iron oxide present in the slag most likely originating from pyritic minerals.

In both diagrams, the data plot along a line showing that, although the amount of iron oxide varies, the ratio SiO_2/Al_2O_3 remains relatively constant. In addition to the scarcity of residual, i.e. non-reacted, grains and the low melting temperature of the slag, this seems to suggest a good control of the charge proportions.

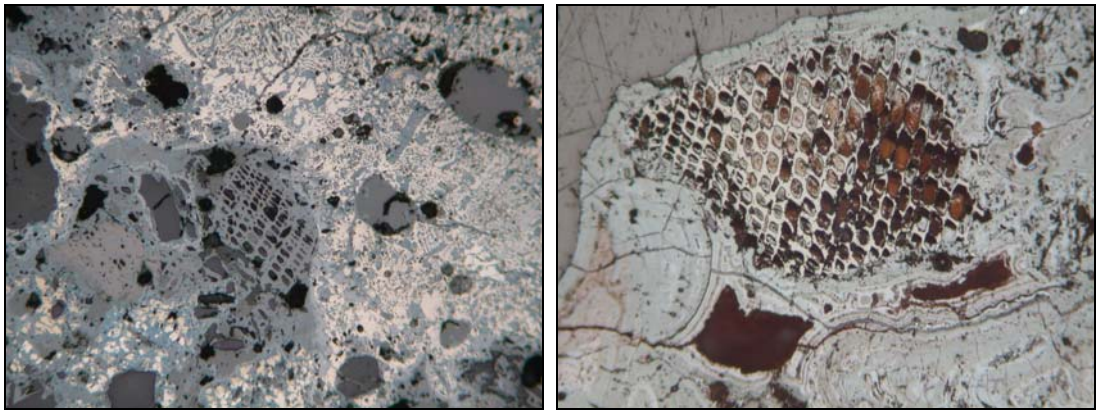


Fig. 6.55. *Pieces of charcoal trapped in samples of matte (left) and slag (right) (optical microscope, plan polarised light, 100x, long axis ~1 mm).*

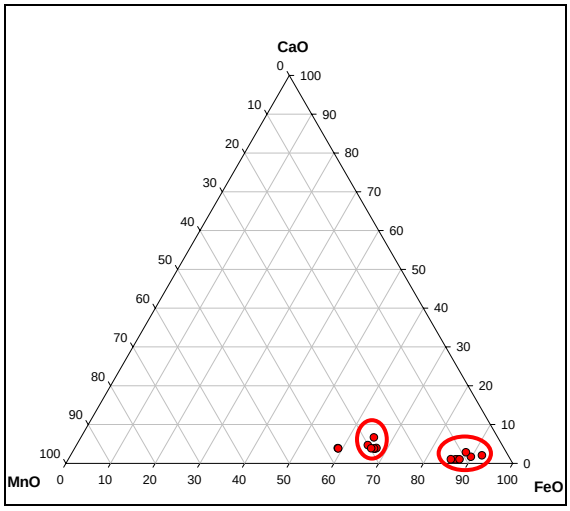


Fig. 6.56. *Diagram plotting slag samples on the ternary system MnO-FeO-CaO showing the greater variation in concentrations of MnO.*

The macroscopic study of pieces of platy and 'channel' slag has clearly documented that the slag produced during smelting was tapped. The tapping of slag would not be an unusual process, since this technique is advised by contemporary authors for various gold, silver and copper ores (Hoover and Hoover 1950: 381-396; Sisco and Smith 1951: 235, 251; Smith and Gnudi 1990: 148) and most smelting furnaces are described to be built with tap-holes to allow for possible slag tapping (Fig. 6.52). In addition to these historical sources, although there is no other archaeological evidence of early modern gold smelting, slag tapping has been commonly documented at various similar sites of the same period and earlier.

The analysis of the slag samples has revealed that their composition is overall fairly similar and that they are relatively standardised – and the similar regularity of the matte will be presented below. This seems to suggest that the charge and other smelting parameters were reasonably controlled and did not vary much. This appears as a contradictory statement to the wide variety of minerals exploited, which, on the contrary, would probably produce less standardised slag. It seems from the study of the various raw materials and the consistent products that either the ores exploited came from a complex vein, but always from the same ore, in which the proportions of minerals would therefore be the same, or that the smelters were using a more homogeneous ore vein, and the ore samples studied for this research may indeed not be representative of the materials processed at this site. Another explanation may be an accurate control and weighing of the various types of minerals to be smelted, i.e. lead- and iron-rich ores, with a known quantity of quartz-rich gangue fragments.

6.5.3. Matte: formation and potential recycling

The existence of the matte layer among metallurgical waste is indicative of the smelting of sulphide-rich ores. There are two explanations to the formation of matte: its occurrence among waste materials could either be due to the nature of the sulphide-rich ore itself not being completely roasted prior to the smelting, or to the addition of pyrites or pyritic minerals used as fluxes in the smelt, as suggested by Agricola (Hoover and Hoover 1950: 234) and Ercker (Sisco and Smith 1951: 105). It seems from the study of this site that a combination of both situations could actually be documented here: the ores from the Gastein area appear to be self-fluxing, their pyritic minerals and iron carbonate-rich gangue naturally balancing the quartz-rich gangue, if used in appropriate proportions. The ore mixture could therefore be both the raw material and the flux. It is however not impossible that fragments of gangue, either rich in quartz or iron – or both – may have been added to the charge to help the formation of slag, whenever required to initiate the fusion of the charge or to control its state and behaviour in the furnace, for example when it did not start to melt or when, once molten, it was not reaching the desired fluidity and could have subsequently hindered the tapping. A similar self-fluxing mixture of sulphidic ores leading to the formation of lead, matte and slag, had also been identified linked to the ancient exploitation of silver in south-west Spain, with the clear distinction that a layer of speiss additionally formed between the lead bullion and the matte in the latter reaction (Keesman 1993). The smelting operation documented in the Angertal only showed small and rare inclusions of antimonides, and possibly some arsenides.

Roasting, as previously explained, is a very frequently – almost always – recommended step with which to start when processing sulphidic ores (Hoover and Hoover 1950: 276; Sisco and Smith 1951: 102, 109). In the case of roasting taking place in the Angertal, the presence of matte is more likely to be explained by the addition of sulphidic fluxes. No archaeological evidence of roasting pits or areas at the excavated sites have been discovered, either in the mining area or at the smelting site. In any case, as seen above, it may not have been necessary to roast the ore since the components of the various minerals would have made the whole mixture self-fluxing. Besides, although sulphur has to be removed from the ore itself to allow an easier and more efficient release of the noble metals, it appears to be necessary and recommended by all three authors, Biringuccio, Agricola and Ercker, to add some

sulphidic material, such as galena (Smith and Gnudi 1990: 153), antimony sulphide, pyrite or "cakes made from pyrites" (Hoover and Hoover 1950: 396-400) to the charge in the furnace in order to deliberately produce matte. Ercker advises to smelt gold concentrates obtained after amalgamation with pyrites to form some "slag-matte" (Sisco and Smith 1951: 103-105). Biringuccio and Agricola describe the tapping of matte into the forehearth in addition to the slag and bullion (Hoover and Hoover 1950: 381; Smith and Gnudi 1990: 153-154, cf. chapter 4). At first glance, there seems to be a contradiction in the statements of these sixteenth-century authors, when recommending the introduction of sulphidic compounds as fluxes in their furnaces to intentionally create a matte layer in between bullion and slag, while also advising in different parts of their treatises the systematic roasting of sulphidic ores. This may be related to the kinetic and thermodynamic conditions of the reactions taking place in the furnace at high temperature. It may be possible that the noble metals are more easily released and then collected by lead if the ore has been initially roasted and its structure consequently weakened and oxidised, but that having a layer of matte form in between slag and metal strengthens the reducing conditions at the bottom of the furnace by acting as a cover, and reduces the amount of noble metals potentially going into the slag by facilitating the mechanical separation between the lead phase and the low-viscosity slag. There is however a downside to the formation of matte, since silver can partially and quite easily get trapped in this phase and therefore be lost, which would then mean that further processing of this phase would be necessary to retrieve it.

Matte also gives information about the redox conditions in the furnace. The oxygen pressure in the furnace would have been lower than in the situation of sole slag formation, since an equilibrium between sulphur in the oxidation state –II and sulphur dioxide, where the oxidation state of sulphur is +IV, was created during smelting for both sulphide- and oxide-rich phases to coexist. The presence of matte indicate that the conditions were very reducing in the furnace, and probably more so at the bottom of the furnace, thus facilitating the collection of the noble metals by the pool of metallic lead and potentially reducing the proportion of lead metal being oxidised and vaporised or lost in the slag phase.

The occurrence of matte being apparently smaller than that of slag in the archaeological record[6] of the Angertal may suggest that the former was possibly re-smelted. This could have been added as the main raw material with suitable fluxes, in order to extract the precious metals which would have remained trapped, or recycled as an additive in subsequent smelts of ore minerals for the same purpose. In earlier studies, it has been argued that matte could start forming when the ore contains at least 2% of sulphur (Kassianidou 1998). This suggests that the smelting of pyritic and more generally sulphidic ores would lead to a consistent production of matte with every smelt, leading to the production of a substantial total quantity of matte. The relatively small amount of matte found further confirms the likely possibility of matte being processed in subsequent smelting operations. Although we have not found direct evidence of the recycling of matte in order to retrieve the noble metals within it, the relatively high levels of silver detected in the analysed matte samples (0.5 wt% Ag on average), and the production of a gold-silver bead from the cupellation of one matte sample, bring up the question of whether the Angertal smelters were aware of that loss, which would be in favour of its recycling.

A good incentive for the re-use of matte would have been if fragments had been regularly quantitatively analysed using fire assay, as has been done experimentally on several archaeological samples, and for which potentially significant concentrations of silver – and maybe gold – could have be found. The potential loss in precious metals in matte has clearly been documented in Oberstockstall, and this phenomenon is likely to happen on a larger scale as well, as has been shown by the experimental cupellation of matte fragments. Although the process appears to be more standardised in the Angertal, it should have been more easily controlled on a smaller scale. It is therefore not surprising to notice a loss in precious metals in blast furnaces, if such a phenomenon was also taking place on the crucible scale. There were however different concerns in the laboratory of Oberstockstall, which was not oriented towards a standardisation of a specific process. It would not be surprising if the smelters in the Angertal were actually recycling matte by melting it again in a furnace, when it has been suggested that the individuals in Oberstockstall were occasionally scorifying it on a smaller scale, maybe with the same intentions or for more general research purposes. As previously described (cf. chapter 4), Agricola

[6] See footnote 1 on page 188.

advises to pile up a large quantity of matte from several smelting operations and then re-melt this accumulation of matte 'cakes' in the furnace to collect its content in noble metals, or as soon as these 'cakes' have solidified to directly put them back in the furnace (Hoover and Hoover 1950: 381-382, 386). Biringuccio also recommends the re-processing of matte, either by smelting it in the same way as the ore or by liquation (Smith and Gnudi 1990: 155-158). The smelters of the Angertal may have been aware of these procedures and known that they could have been performed at other contemporary production sites. This may have prompted them to carry out a similar recycling operation. The narrow variation in the slag samples analysed indicates that, if matte were indeed recycled, it would have been as an additive to following ore smelting operations, as the recycling of matte on its own would have generated slag of different compositions. This matte recycling issue is further discussed in the following section below as well as in the next chapter.

6.5.4. Silver and gold in ore, bullion, matte and slag

The lead bullion clearly acted as a collector for the gold and silver at the bottom of the furnace. Antimony also preferentially went into this metallic phase. The lead content of the slag for many of the samples, in the order of 1 to 10 wt% with an average of *ca.* 5 wt% PbO, is typical of medieval to early modern galena smelting (Rehren *et al.* 1999). The metallurgy of silver is inextricably linked to lead, and in many cases to copper in central European exploitations of the early modern period. In fact, it can appear difficult to differentiate between the two types of exploitation. Compared to earlier medieval extraction of silver-lead-copper from polymetallic sulphidic ores in the Black Forest (Goldenberg 1993), the slag shows relatively high lead and similar copper contents, which could indicate the mining of silver-rich galena and involve some production of copper (Table 6.2, p. 208). The overall concentrations in lead and copper detected in the ores (Table 6.1, p. 204) however suggest that galena may have been present to some significant extent among the variety of smelted minerals, while copper-rich minerals, such as chalcopyrite, only represented a minor fraction of the potentially smelted ores. A good example of the smelting of lead-rich ore can be noticed in sample AN 134a-03 (Fig. 6.24, p. 212), where relatively large areas of partially reacted galena have been identified together with forming slag. The mixture of ores may have contained lead in sufficient

quantity to act as a collector for the noble metals, so that any further addition of metallic lead to the charge may not have been necessary. Such a situation has been conjectured for the Roman gold smelting of Três Minas, but the occurrence of lead ingots at that site seems to indicate that lead metal was indeed added to the charge (Bachmann 1993). Similarly for the Angertal, it appears from historical sources that lead metal was brought from nearby regions, such as the Bleiberg in Kärnten, to be specifically used in the smelting of gold and silver ores (Gruber 2000: 164), therefore probably suggesting that lead metal was added relatively regularly to the charge to collect the noble metals.

The archaeological lead cupelled in this study yielded around one percent of the weight of the initial sample as noble metals (Table 6.9, p. 224), producing beads or *reguli* composed of silver with around a fourth of gold, as shown by EPMA-WDS and micro XRF analyses (Table 6.10, p. 229). Thus, there would have been around 7.5 g of silver and 2.5 g of gold per kg of lead bullion created. Although the gold constitutes only about one quarter of the regulus by weight, it was the main value metal due to its higher price. Silver would have been a valuable by-product to be traded as well.

It is relatively difficult to estimate the richness of the ore smelted during the sixteenth century. The best approach seems to relate the gold and silver quantity in the archaeological bullion to the amount of ore from which this was extracted. Thus, one needs to quantify the amount of ore that would have been required to produce one kilogram of lead bullion, containing about 10 g of gold and silver. This is difficult since the average galena content of the furnace charge is unknown; nonetheless, for the purpose of the following calculation we initially assume that the amount of lead bullion produced by one smelting operation corresponds to 10% of the original weight of the smelted ore. We will also hypothesise that this bullion contains all the gold and silver originally included in this ore. Although we know that some precious metals are lost in the matte (see below), this simplification allows us to roughly estimate the overall content of precious metals in the ore at *ca.* 1,000 ppm (one tenth of the 10,000 ppm gold and silver found in the archaeological bullion), made up of *ca.* 750 ppm of silver and *ca.* 250 ppm of gold. This means that the ore would contain *ca.* 750 g/ton of silver and *ca.* 250 g/ton of gold. This compares to concentrations of gold ores exploited after the 1980's, which contain between 4 and 9 g/ton of gold, with very rare amounts above 15 g/ton (Edwards and

Atkinson 1986: 147). Similarly, the Roman mines of Três Minas in Portugal provided ores, which have been estimated to yield *ca.* 15 g/ton of gold and *ca.* 200 g/ton of silver (Bachmann 1993). This would indicate that these mineral deposits, locally exploited in Gastein in the sixteenth century, were exceptionally rich in precious metals especially in gold – presuming our initial assessment of the amount of lead produced is not too far from actual practice. However, written sources give the gold content in the ore exploited in Gastein during the second half of the seventeenth century (the earliest period for which specific data are available) to be 36.6 g/ton, which already corresponds to the declining period of the mining in this region (Gruber 2000: 174). It is further stated that the extracted ores yielded 28.5 g/ton of gold between 1760 and 1779, and that this amount was half the yield achieved for the year 1569 (Gruber 2000: 175). This textual information indicates that the ores exploited in that specific year of the sixteenth century yielded an ore containing between 50 and 60 g/ton of gold. Assuming that this concentration of gold represent between 20 and 30% of the combined amount of precious metals, it is possible to estimate the silver at 150-240 g/ton, resulting in a total of 200-300 g/ton of precious metals in the ore, for the main period when the Angertal smelter was active. The amount of gold inferred from historical sources represents roughly five times less the level estimated from the previous calculation (250 g/ton gold), but remains relatively high compared to the values of 4-9 g/ton and 15g/ton from twentieth-century and Roman deposits respectively (Edwards and Atkinson 1986: 147; Bachmann 1993). In return, this yield implies that instead of obtaining 10% of bullion, only around 2%, i.e. 2 kg of bullion per 100 kg of ore were produced. This figure of 2 % lead bullion yield from the ore appears reasonable from a technical point of view, and will be used for the following calculations. The gold and silver content of the bullion remains unchanged, but the amount of bullion produced per unit of ore is now only about one fifth of the previous estimate, thus the ore was probably less rich, too, by the same factor of five. Although much lower than the initial estimate, the revised figure of around 50 g/ton gold is still high compared to other mines. The relative richness of the ore in gold and silver could also be further implied by the economic context of the time and the fact that great quantities of precious metals were arriving from the New World. In a similar way to contemporary delocalisation of production, it probably became easier and cheaper to transport the precious metals produced and traded in the Americas than smelting ore

minerals on the European continent. In order for an exploitation such as the Angertal to keep on being financially sustainable and profitable, the yield of precious metals obtained from ore smelting most likely needed to be fairly high.

The analyses done as part of this thesis also allow to estimate the overall loss of noble metal during the smelting operation. Most slag samples have gold and silver below the detection limit of the XRF instrument, and there is virtually no metallic lead trapped in the studied slag samples. Thus, it is assumed that the slag is practically free of gold and silver. However, the cupelled matte generated beads weighing around 0.1 % of the matte weight, one tenth of the concentration found in the lead bullion. The quantity of noble metals therefore lost in the matte appears on average ten times lower than the amount recovered from lead bullion, which would equate to a total noble metal yield of c 90%, giving the impression of a relatively small loss in the matte. However, the amount of matte produced during each smelt would have been much higher than that of bullion (estimated at 2 percent of the weight of the ore charge), which would therefore increase considerably the potential losses in precious metal. No reliable figure exists for the relative ratio of slag to matte in the main slag dumps at the Angertal; however, matte does not seem to be extremely rare (B. Cech, *pers. comm.*). For the sake of this discussion it is assumed that in addition to the 2% lead bullion about 10% of the ore charge was returned as matte, the remaining 88 wt% of the charge being lost as fumes and vapour, and as slag. Assuming thus that five times as much matte was discarded than lead bullion produced, this would increase the loss of noble metal into the matte to half the amount (five tenths rather than one tenths) of the noble metals recovered in the bullion, indicating a total noble metal yield of only two thirds, and a total loss of one third. Furthermore, the concentration of noble metals in the matte, at an average 1,000 ppm (0.1% of the matte), is about four to five times higher than the estimated total noble metal content in the ore, at *ca.* 200-300 ppm. There is a clear incentive to further process the matte to extract this noble metal content, and not to let it go to waste.

However, the proportions of precious metals in these beads were different from those in the bullion – except for one sample of lead. Two matte samples yielded around 25 mg of gold and 975 mg of silver per kilogram of matte AN 104-01 (equal to 25 ppm Au and 975 ppm Ag), and around 1 mg of gold for 999 mg of silver per kilogram of matte AN 108-04, equal to 1 ppm Au and 999 ppm Ag (Fig. 6.57). Thus,

the matte is proportionately much richer in silver than gold, with the gold concentration being only a fraction of the gold level in the ore.

Thus we hypothetically consider that for 100 kg of ore – which would contain roughly 5-6 g of gold and 15-24 g of silver –, the smelting process produced 10 kg of matte and 88 kg of slag, in addition to the estimated 2 kg of bullion[7]. The 2 kg of bullion would contain approximately 20 g of precious metals, divided between 15 g of silver and 5 g of gold, while 10 g of noble metals with 9.75 g of silver and 0.25 g of gold would go into the matte. From this simplistic calculation, the yield in gold and silver would reach 95% and 60% respectively for the bullion, the loss being therefore 5% and 40% respectively for gold and silver in the matte. These values could suggest that the discard of the 10% of matte produced by the smelt may have been acceptable by the smelters of the Angertal, as only 5% of the original gold content of the ore would remain trapped in it, while 95% of this gold would be collected in the lead bullion. As mentioned above, the real proportion of matte within the slag heaps is unknown; it may well be less than the 10% assumed here (B. Cech, *pers. comm.*), in which case the losses would be accordingly lower. The regular presence of matte in the slag heaps indicates that the recycling of matte to the point of complete avoidance of matte formation may have not been a relevant operation to carry out, considering that it would have required significant additional resources such as fuel and labour, and that its richness in iron would have required an increase in silica in the charge to maintain a fluid slag regime, further adding to the quantity of slag produced and fuel consumed. The loss of 40% of the total silver initially present in the charge into the matte (or an accordingly lower proportion, if the total proportion of matte was less than ten percent of the ore charge) may therefore suggest a compromise between some recycling of matte to avoid too large quantities to form, and complete recycling at the expense of increased slag formation and fuel consumption.

At face value, nearly 1,000 ppm silver in matte not only represents a relatively large fraction of the total silver content of the ore, but makes it rich even compared to common pre-modern silver ores (Rehren *et al.* 1999; Rehren *et al.* 2002). This clearly makes the recycling of matte in smelting operations worthwhile, not least

[7] There were most probably some losses as fumes and vapour during the process, which would make the balance of products less than 100% of the original charge. These losses have been ignored for the purpose of this basic calculation.

since matte did not need any preparation compared to the ore, and could have thus been readily smelted in subsequent furnace charges, added to the ore mixtures. Of course, taking such a decision would have to be based on relatively precise knowledge of the total silver and gold content in the matte; as mentioned before, a useful tool for the quantitative assessment of the matte would have been fire assay, as documented for the small-scale Oberstockstall laboratory (cf. chapter 5).

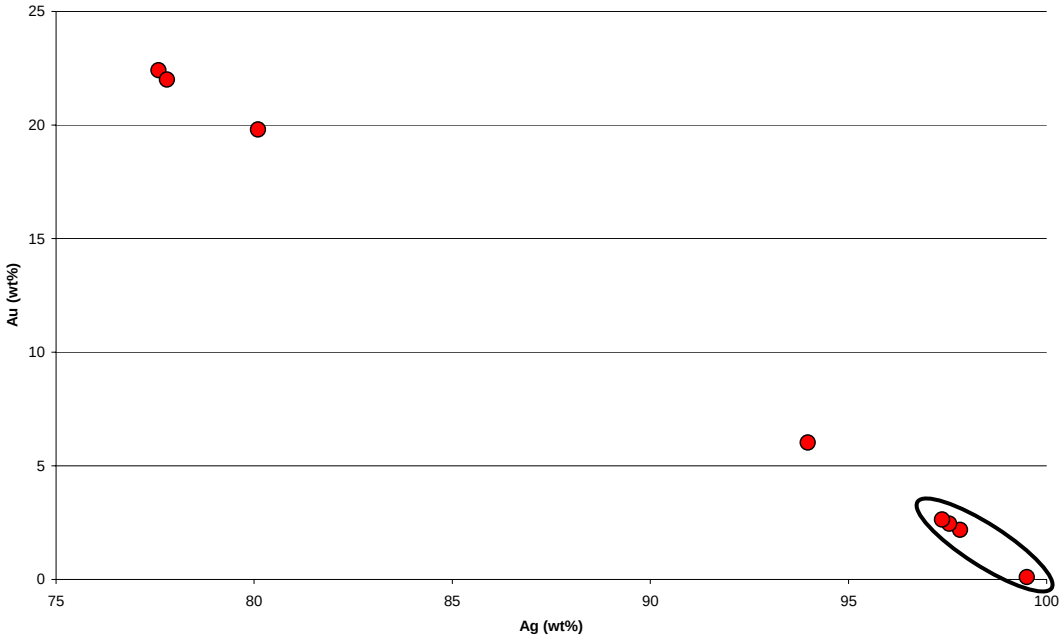


Fig. 6.57. *Diagram of gold vs. silver concentration, clearly displaying the difference in gold content between cupelled samples of lead and matte (circled).*

6.5.5. Reaction between technical ceramic and charge

As expected during a smelting operation, the surface of the furnace wall has partially melted and reacted with the charge, contributing to the formation of fayalitic slag. The SiO_2/Al_2O_3 ratio decreases from *ca.* 4 in the non-vitrified ceramic fabric to *ca.* 3 on average in vitrified areas. Some alumina will react with the molten charge to participate in slag formation, but feldspars being less chemically refractory than alumina and generally clay, are more likely to react preferentially with the melted components of the charge. The SiO_2/Al_2O_3 ratio therefore indicates a depletion in silica in vitrified zones of the furnace wall. These vitrified areas are relatively rich in iron compared to the non-vitrified ceramic fabric, the SiO_2/FeO ratio ranges between *ca.* 6 and 28 with an average of *ca.* 15 in vitrified regions of the sample, compared to *ca.* 41 for the ceramic. Iron is readily available from the

sulphidic minerals or from the gangue, although if some sorting has occurred, the proportion coming from the gangue should be rather limited, quartz being selectively kept to balance iron-rich sulphides and assist their fusion. Iron could also come from recycled matte from previous smelting operations, in the case of this phase being indeed re-smelted. A similar pattern can be seen for potash, magnesia and manganese oxide, for which the same ratio dramatically drops in the vitrified fabric, showing a relative enrichment in these various elements, and further highlighting a depletion in silica in these areas. Potash and magnesia most likely come from the charcoal ash, with potash also partially contained in molten feldspar from the furnace wall; while, as explained above, manganese oxide most certainly originates from the ore, where it is present in the iron carbonate-rich phase of the gangue. The SiO_2/Na_2O ratio, in contrast, increases from *ca.* 15 to between *ca.* 15 and 28 with an average of *ca.* 21, showing a loss in soda in the vitrified furnace wall fabric. Being highly volatile at high temperature, soda may not have withstood the heat achieved in the furnace and would have partially vaporised; however, such low concentrations may also on the whole illustrate a dilution of this element due to the added base metal oxides, such as those of iron or manganese. Overall, the furnace wall partially melted during the smelting, and the ceramic reacted with the charge, losing some silica, alumina and soda, and incorporating some elements of the charge into the vitrified surface. It has not been possible to determine whether the furnace wall was originally lined with a different material such as lute, as depicted in Agricolal's *De Re Metallica* (Hoover and Hoover 1950: 376, 378), mostly because of the intense vitrification of the samples available.

6.6. Summary of the archaeometric study of the remains from the Angertal smelting

From the interpretation of the results of the archaeometric study of excavated materials from the Angertal associated to large-scale metallurgical activities, it has been possible to reconstruct the overall process used by the smelters to recover the noble metals, especially gold, possibly from a variety of locally exploited sulphidic minerals. This smelting process was carried out in three blast furnaces, producing characteristic fayalitic slag, matte and lead bullion. The latter collected most of the precious metals, with a fraction, however, partially remaining in the matte layer.

Several issues were discussed which do not seem to get a definite answer, such as the absence of indicators for arsenopyrite in waste products, which could potentially appear contradictory to written sources and previous research, or the possible re-use of matte to recover the noble metals trapped. The Angertal smelting site was supplied in minerals rich in precious metals by the surrounding mines. From the analytical data, it is however not really possible to establish whether each smelting site would be associated to a specific mining site or a specific metal. If it were not for the historical sources, which repeatedly report the connections between the two mines of the Bockhart and the Erzwies with the smelting site of the Angertal, it would remain difficult to precisely determine the provenance of the ore in terms of mining site, because of the strong similarity existing between the ores found at both the excavated site of the Bockhart and the surveyed site of the Erzwies, and in the region of Gastein more generally – and also because the ores studied for this research may not be representative of what was smelted in the sixteenth century. From the wide range of minerals identified at the Angertal from pieces of ore, and possibly processed as shown by the analyses of waste products from smelting, there does not seem to be any clear association between smelting site and type of ore, although arsenopyrite has not been noticed at the studied site in as high a quantity as could have been expected. As already mentioned, an alternative to this lower occurrence of arsenopyrite as a potential smelting raw material could be the smaller concentrations of precious metals in this particular mineral. This poor content in gold and silver may have led to the deliberate disregarding of this mineral during mining in the sixteenth century.

The lead bullion produced by the Angertal smelting has been suggested to contain at least *ca.* 7.5 kg/ton of silver for *ca.* 2.5 kg/ton of gold, while the matte would include *ca.* 25 g/ton of gold for *ca.* 925 g/ton of silver. The silver and gold contents of the ore could be estimated between 50 and 60 g/ton of gold with 150 to 240 g/ton of silver. It has been speculated that nearly all the gold would have been collected by the bullion, whereas silver would have been almost equally divided between bullio and matte. The *ca.* 3:1 ratio of silver to gold in the ore noticed in the cupellation beads of bullion samples is in good agreement with historical sources, which report between 20 wt% (Gruber 2000: 165) and 30 wt% (C. Bartels, *pers. comm.*) of gold contained in the silver. The cupellation of matte has shown that it may appear to contain relatively high amounts of silver, which may have required

further smelting. For the smelters of the Angertal to be aware of the loss that was occurring along the process, they may have needed to assess and quantify it by fire assay of matte in order to decide whether it was worth recycling this waste material. From the results of the cupellation experiment performed within this research, it could be argued that matte was indeed worth processing further for its content in noble metals, as the amount lost in matte does not appear to have been on the whole that negligible.

The next chapter will discuss these data in its broader historical context in an attempt to understand the organisation of the site and estimate the level of standardisation and efficiency of the process. The results from the study of this particular site will also be compared to those from its contemporary small-scale counterpart in Oberstockstall. The reconstructed processes of both sites fully explained in chapters 5 and 6 will further be contrasted to their theoretical descriptions from contemporary metallurgical treatises, and see how they fit within the overall historical and social context of their time.

Chapter 7 – Small scale vs. large scale: laboratory research vs. industrial production in sixteenth-century Central Europe

The two previous chapters have presented the results of the archaeometric study of the archaeological material from the two sites of interest, the laboratory of Oberstockstall and the smelting site of the Angertal. The aims of this chapter are to now place the interpretation of these scientific data within their historical context and compare them to each other and to information from their contemporary written sources. In so doing, I hope to establish a more complete picture of the metallurgy of noble metals in Europe during the early modern period, and more specifically in this region at a time of major metallurgical production. Emphasis will be placed on the similarities and discrepancies noted between the two sites operating on a clearly different scale and for distinct purposes. The second focus of this chapter will be the comparison between the information acquired from archaeological evidence and Renaissance technical treatises. This comparison has already been initiated, where relevant, in previous sections of this document, and it will be used more systematically here to explore and try to understand the intentions and potential reasons behind certain technological choices.

7.1. The laboratory of Oberstockstall: routine fire assaying or innovative research and development?

7.1.1. A unique context for laboratory-scale metallurgical reactions

The unique archaeological assemblage from the laboratory of Oberstockstall has given a picture of a relatively closed and secretive place, where metallurgical and chemical operations were routinely carried out in the context of the fire assay of ores. As shown in chapter 5, a main three-step *modus operandi* related to the fire assay of fahlores, possibly associated with other base-metal sulphides, and probably containing some precious metals and having grown in a gangue of calcite and/or quartz, has been identified, amongst a variety of other activities. In addition to the various diagnostic technical instruments, a choice of typical substances employed in a laboratory, such as salt, saltpetre, iron filings, metal sheets, were also identified.

It may be important to remember here that the material studied for this project focused on very specific reaction vessels and metallurgical products, and in fact only represents a fraction of the assemblage from Oberstockstall, and even less of what might have been in use before the destruction of this laboratory. The two pits excavated in 1980 and 1993/1994 by von Osten (1992; 1998), where all the artefacts have been found, are not likely to have been used on a daily basis by the chymist(s) working in the laboratory to discard broken vessels or unwanted materials. Indeed, there are too many undamaged and unused ceramic wares for this pit to have been an everyday waste deposit for this laboratory. It seems rather that this deposit was created when the activity in the laboratory of Oberstockstall ended. This would, for instance, further explain the absence of conical vessels, into which crucible fusion products are thought to have been poured to cool – when not left in the triangular crucible itself –, as these containers would have been broken to retrieve the solidified bullion and the resulting ceramic fragments subsequently thrown away in a common area for all the everyday waste material of the laboratory (Fig. 5.32, p. 150). The same explanation could be applied to the pieces of slag produced in the triangular crucibles: none have been found but one, suggesting that the main bulk of this type of metallurgical waste has been discarded elsewhere. Besides, the excavated area is located in the centre of the room used as a laboratory in the sixteenth century, and would mean a very awkward location for an everyday waste pit, and very inappropriate for the daily activities carried out there. The precise position of the daily waste pit is still unknown but it was most certainly situated outside the sacristy, and probably even outside the building. It has been mentioned previously that, due to various reasons, such as recycling, the quantity of one type of archaeological artefacts recovered through excavation may not be representative of the actual overall amount produced in the past and therefore not reflect the actual situation as it was. This is not only a general problem but can be applied to the more specific space of the excavated site itself, as can be seen in the case of Oberstockstall – and of the Angertal. However, though we may not acquire a full view of the multiplicity of the activities taking place at this site and their respective quantitative importance, a good panorama of their range can be reconstituted.

This diversity of procedures suggests that, even if some routine fire assay of ores was carried out, there was more to this laboratory than pure technical and analytical assessment of raw materials. The real question behind the overall function of the site

of Oberstockstall lies in the intentions and purposes of the individuals, who actually set it up and ran it on a possibly regular basis. As previously mentioned, the historical context of most of the known laboratory remains is generally easily explained and the purposes of their activities clearly identified. Fire assay, in particular, has been acknowledged in obvious contexts of mining and smelting, i.e. the assaying of ores (Schifer 1998; Unglik 2000; Bailly-Maître 2002; Beaudoin and Auger 2004; Thomas *et al.* 2006), and related to the minting industry (Jeanjacquot 1993; Bayley 1996; Saunders 2001). On the contrary, although it was possible from the archaeological evidence to reconstruct several of the high-temperature metallurgical procedures carried out in Oberstockstall, it has proved difficult to understand the "intentionality" of human beings behind the materials and their utilisation. The fact that this laboratory was located – possibly hidden – in a sacristy and its owners were parsons may further emphasise the possible secrecy of the whole affair – and its possible partial illegitimacy –, and may explain why it remains very intricate to interpret its context. It is indeed possible that the users of this laboratory were not only assaying in quantitative terms but were also testing the behaviour of different reagents or unknown substances. It is worth reconsidering here the historical evidence regarding the likely users of the laboratory, together with our understanding of Renaissance chymistry, which made it perfectly compatible to carry out 'scientific' experiments whilst believing in the transmutation of matter and other concepts that would nowadays seem unacceptable. All potential owners and/or users of this site were known to be interested in metallurgy and chymistry, among other 'scientific' topics of the time. As noted before, the Fugger brothers belong to a German family of miners and metallurgists, and were probably involved in this field before being assigned to the parish of Kirchberg am Wagram, and simultaneously showed interest in chymistry. On the other hand, the first of these individuals, Christoph von Trenbach, is also famous for having accumulated a huge debt at the local apothecary, due to his ordering of a large number of chemicals, while his younger brother showed a strong interest in Paracelsus and studied divination arts, now regarded as pseudo-sciences. This could actually denote an "ambition" or intention, which goes beyond the provision of a commercial service. It is therefore possible that research related to precious metals was taking place along more mundane metallurgical activities, such as the common fire assaying of ores. It is known that "chymists" of the Renaissance combined experiments related to

transmutation with other tests aimed at developing more efficient metallurgical techniques. These aspirations were not mutually exclusive, contrary to present-day anachronistic assumptions (Martinón-Torres and Rehren 2005a), and it was not inconceivable for "chymists" to believe in Aristotle's theory of the four elements and at the same time carry out experiments worthy of modern scientists.

The 'R&D' aspect of this site is further indicated by the identification of 'unknown' substances, such as antimony, which has been identified in the majority of the samples analysed, and bismuth, more sporadically detected but in significant concentrations. For several specimens of crucible and scorifier slag, the detected levels of antimony were too high to consider that this element would only originate from an antimony-rich ore, especially when these were combined with very low concentrations of lead oxide (Table 5.1, p. 121 and Table 5.7, p. 165). As seen in chapter 5, it is possible that antimony sulphide was sometimes added to the charge, in order for the antimony to act as noble metal collector instead of lead, but this would have been unusual. In the sixteenth century, the nature and properties of antimony and bismuth were not fully understood, and it is possible that these metalloids were still considered special types of lead (Hoover and Hoover 1950: 428-429, *footnote*). While it may be that antimony and bismuth were simply mistaken for lead, it is more likely plausible that experiments were being conducted here in order to understand better the properties of matter and new elements. This change in collector may therefore have been intentional, with the meaning of testing the properties of this metalloid resembling lead but at the same time in some ways perhaps noticeably different. This substitution could have allowed the chymist to study whether both elements would behave in similar ways when submitted to the same high-temperature process, with identical reaction parameters and starting reagents.

It seems appropriate to introduce at this stage of the discussion two metallic fragments, a tin-rich lump and a large half-spherical piece of lead, found within the archaeological record and adding somehow a fairly puzzling feature to the whole picture (Fig. 7.1-7.2). The SEM-EDS analysis of a small mounted specimen from the surface of this half-sphere of lead shows that it contains nothing but lead metal, with red and yellow crystals of litharge and massicot on its surface due to some corrosion. The most interesting features of this piece are the numerous grooves visible everywhere on its surface, for which no satisfactory explanation has been reached

yet (Fig. 7.1). The second partially re-solidified lump has no other equivalent in this assemblage; it is overall very rich in tin and composed of a mixture of metal, matte and slag. The metallic areas consist of a matrix of pure tin metal, in which are found harder elongated crystals of tin-lead sulphide (*ca.* 62 wt% Sn, 19 wt% Pb, 19 wt% S), copper-tin alloy with some nickel (*ca.* 1 wt% Ni), and dendrites of lead metal including small amounts of tin (*ca.* 3 wt% Sn). The matte areas show phases of the same composition as the inclusions of tin-lead sulphide noticed in the tin matrix, pyrrrhotite with low amounts of copper and tin (*ca.* 1 wt% Cu, 1 wt% Sn), and an iron-tin oxide (*ca.* 59 wt% Fe, 12 wt% Sn). The relatively high overall iron content of the matte areas and the occurrence of pyrrhotite link this sample to the rest of the assemblage, the abundance of tin in this sample however remaining fairly bewildering. Could this be the resulting product of a failed attempt at assaying a different sulphidic ore, which would have been richer in tin, e.g. stannite (Cu_2FeSnS_4)? Stannite is, however, rare and not a mineral known for its containing precious metals. Was this a trial at actually extracting the tin from an ore? Or using tin as a noble metal collector, in a similar way to antimony? One of the alternative names for tin was “white lead” and its properties had not been fully explored nor its metallurgy properly explained prior to Agricola’s text, outside the well-known fact that it was the main alloying component with copper in tin bronzes and that such an alloying operation would harden the copper. This operation may therefore be part of this wider set of experimentations on substances.

In the long term, experiments such as those performed in Oberstockstall would allow a degree of understanding of nature that progressively led to the abandonment of old ideas and ambitions (Principe and Newman 2001), with the segregation of alchemy-chemistry-metallurgy during the eighteenth century. The process of separation of these fields is however not complete in the sixteenth century, hence the chaotic picture of the laboratory obtained from this study.

Fig. 7.1. *Relatively large half-spherical fragment of lead metal, displaying a very weathered surface covered by multiple grooves (scale bar 5 cm, photo: M. Martinón-Torres).*

Fig. 7.2. *Tin-rich lump, showing signs of melting prior to re-solidification (left, scale bar 5 cm, photo: A. Mongiatti), and its microstructure displaying a tin metal matrix with elongated crystals of copper-tin alloy or tin-lead sulphide, and dendrites of lead metal (right, optical microscope, plane polarised light, 200x, long axis ~800 μm).*

7.1.2. Kapfenberg: a secret laboratory similar to Oberstockstall?

Very recently, a similar laboratory assemblage has been excavated, which has brought up comparable material to the laboratory of Oberstockstall, and with which parallels can be attempted in terms of diversity of metallurgical residues and possible intentions behind fire assay activities. The assemblage from this site is currently under study and only preliminary analyses of residues from high-temperature metallurgical reactions have been carried out, hence the impossibility of including it as a proper case study for this research project. Although a complete picture of the operations has not been obtained yet, initial results and interpretation will be introduced here, because of their strong relevance to Oberstockstall.

This site is located at the bottom of a hill on which the chapel of Loreto was built, close to the castle of Oberkapfenberg, south-east of the town of Kapfenberg in

Styria, Austria. The site, excavated in 2005 (Friedl 2006; Von Osten and Friedl in press), is situated in hidden galleries running inside a fortification wall, which have been dated to the sixteenth century (Friedl 2006). One of these brick-lined passages has revealed a small and rather unparalleled square brick structure (Fig. 7.3). Close to this construction, a significant quantity of small ceramic vessels similar to those found in Oberstockstall, namely 35 triangular crucibles (Fig. 7.4-7.5), 7 scorifiers (Fig. 7.6) and 46 cupels (Fig. 7.7), was recovered among several lumps of melted waste materials and other typical laboratory ceramic and glass ware, such as muffles and distillation apparatus (Von Osten and Friedl 2008; Von Osten and Friedl in press). The occurrence of this assemblage next to the small brick structure, together with comparison of the latter to depictions in written sources, suggest that it corresponds to the lower half of an assay furnace. This assemblage is overall very similar to the equipment found in Oberstockstall and generally seems to have been associated with the small-scale metallurgy of precious metals (Rehren 1996; 2001; Martinón-Torres and Rehren 2005b; Mongiatti *et al.* in press). These archaeological artefacts and the metallurgical activities in which they were involved are however later than Oberstockstall, as stamps on the bases of two crucibles suggest a date for this assemblage to the late seventeenth or early eighteenth century.

Fig. 7.3. *Remains of a small brick assay furnace base, approximately 50 cm wide and 40 cm high, located in the gallery inside the fortification wall (photo: M. Martinón-Torres).*

Fig. 7.4. *Triangular crucibles recovered from the Kapfenberg archaeological site. Left: corner fragment of an upper rim, note the shiny black slag, which has formed on its inner surface (KA FN 162). Right: three triangular crucibles of different sizes and shapes (KA FN 166-168) (photos: A Mongiatti).*

Fig. 7.5. *Left: well preserved used triangular crucible (KA FN 164). Right: two matching fragments, the base and one wall of a similar triangular crucible (KA FN 165 and 168) (photos: A Mongiatti).*

Fig. 7.6. *Scorifier from the assaying assemblage, displaying a black slag resulting from high-temperature use (left, photo modified after M. Martinón-Torres), and fragment of a similar scorifier, also displaying a thin layer of black slag on its surface (right, photo: A. Mongiatti).*

Fig. 7.7. *Examples of several cupels found close to the assay furnace (left: KA FN 109, 110, 112, photo: A Mongiatti).*

The residues attached to the inner surfaces of a small selection of vessels dedicated to high-temperature reactions have been analysed, along separate fragments of matte and slag, using the same combination of instruments as previously explained, namely optical microscopy, SEM-EDS and EPMA-WDS. The initial analytical results are outlined here in order to give a more detailed picture of this site, very similar to Oberstockstall, but perhaps in appearance only.

The ceramic fabric of the triangular crucibles analysed here is either graphitic (KA FN 166, 167), similarly to that of many of the crucibles found in Oberstockstall, or rich in inclusions of quartz and potassium feldspars of relatively large size (KA FN 162, 164, 168). The nature of the residues still attached to the inner surfaces of triangular crucibles appears to vary widely, from typical silicate slag to large phases of metallic silver.

The silicate slag usually contains high amounts of silica and iron oxide, with smaller amounts of alumina, magnesia, titania and manganese oxide, and variable concentrations of soda, potash, and metallic oxides, such as the oxides of copper, lead, zinc and antimony. These analyses share strong similarities with the Oberstockstall crucibles slag; these triangular crucibles may therefore have been used for the reducing fusion of ores as indicated by elements characteristic of gangue minerals, which contributed to slag formation. The levels of soda and potash are clearly higher than those generally detected in Oberstockstall, suggesting that they may partially come from fluxes or additives rather than from the raw materials or from the ceramic (molten feldspars) only. These high levels are highlighted by the

presence of newly formed phases of leucite and pyroxenes ($FeCaSi_2O_6$) in the melt (Fig. 7.8). Such sources of sodium and potassium could be rock salt (see the discussion in chapter 5 about the non-correlation of sodium with chlorine due to the low saturation levels of silica glass in chlorines of *ca.* 1 wt%), saltpetre, or, combined with the relatively high amount of lime, even some soda-lime-silica or potash-lime-silica glass. Glassware has been found together with these predominant technical ceramics, and it is possible that broken glass apparatus were recycled as flux in these crucible fusions, as has been suggested for Oberstockstall, if the raw materials were rich in iron and needed silica to be fluxed. The glass matrix of slag in the separate lumps is similar to crucible slag, showing overall even higher calcium oxide content.

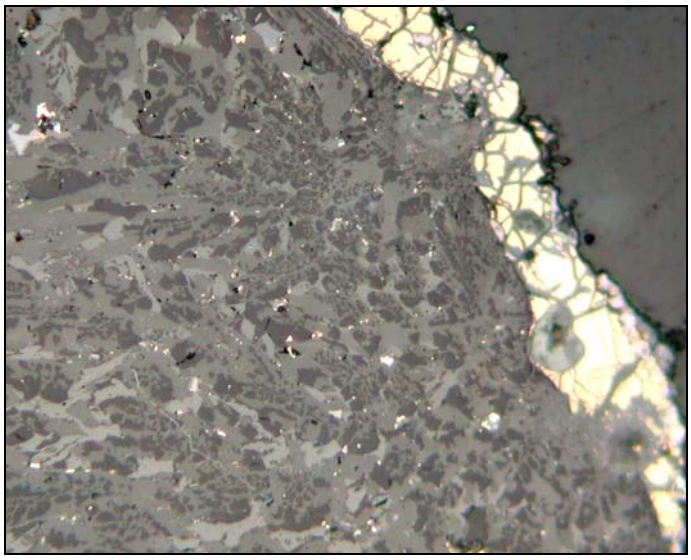


Fig. 7.8. *Matte layer on the outer surface of a slag lump, on top of a pyroxene-rich crucible silicate slag. Note the numerous minute silver prills in the glass matrix of the slag (KA N004/S1, optical microscope, plane polarised light, 200x, long axis ~750 µm).*

The matte in the separate cakes usually includes high concentrations of iron and copper with smaller amounts of lead, and is mostly composed of pyrrhotite, a complex mixture of chalcopyrite with a copper-iron sulphide similar to bornite – indeed showing similar composition to the compound identified in Oberstockstall –, lead sulphide now corroded to lead sulphate, and some copper sulphate (Fig. 7.9). These cakes also frequently display silicate slag phases or inclusions in the matte phases, matching the typical composition of the crucible slag specimens analysed, as well as prills containing antimony and/or lead, and antimony speiss inclusions rich in copper and/or iron, with small amounts of arsenic, nickel and lead (Fig. 7.10). From the slag phases and inclusions in the mixed cakes and the matte inclusions in the crucible slag samples (Fig. 7.8) it is possible to confirm that these separate fragments

were indeed produced in triangular crucibles, through the process of the reducing fusion. By association with Oberstockstall, it can even be stated that the raw material could have potentially been a complex sulphidic ore, such as an argentiferous tetrahedrite fahlore. One difference with Oberstockstall is the clearly greater occurrence of copper in the various oxide-, sulphide- and metal-rich (see below) phases, which could indicate the processing of copper-rich ores as well, such as chalcopyrite. These minerals would have most likely been available locally.

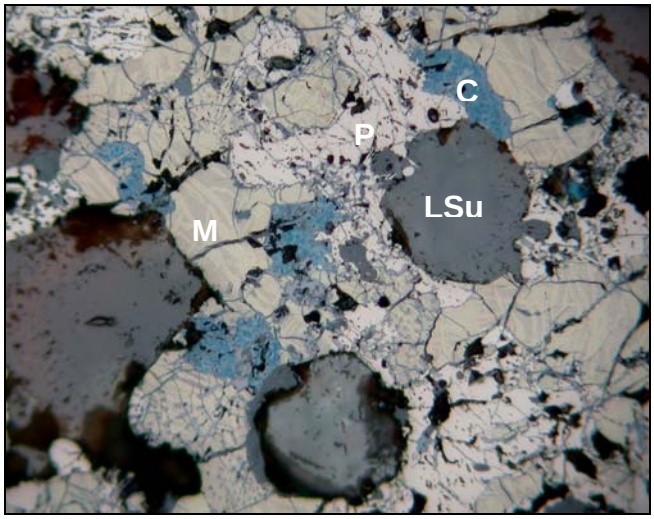


Fig. 7.9. *Typical matte composed of a complex mixture of sulphidic phases, including pyrrhotite (light cream colour, P), striped grains of bornitic sulphide and chalcopyrite (M), grey phases of lead sulphate (LSu) and blue phases of secondary copper sulphide (C) (KA N001/S1, optical microscope, plane polarised light, 200x, long axis ~750 µm).*

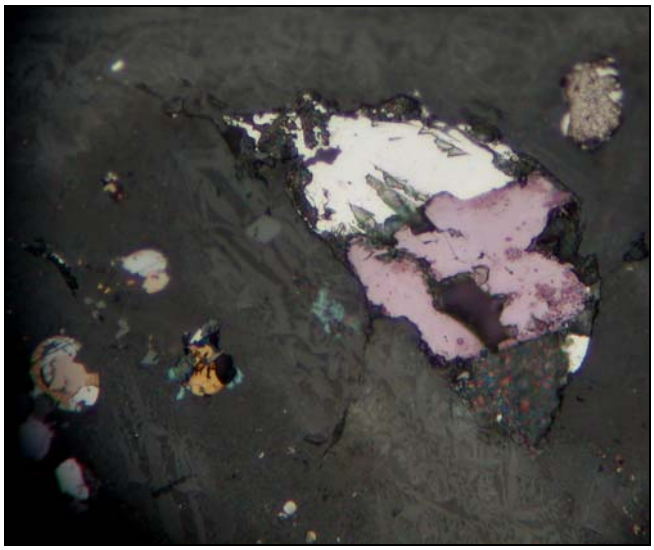


Fig. 7.10. *Bright metal prill with speiss inclusion: antimony metal (white) with copper antimonide (Cu_2Sb, pink-purple) (KA N003/S1, optical microscope, plane polarised light, 500x, long axis ~250 µm).*

If we suggest an argentiferous ore, silver should then be expected as an element of the metallurgical residues. It is in fact present in numerous samples, many silver prills of various sizes have been identified, either as distinct bright phases in the bloated vitrified surface of the ceramic or in the slag, usually at the interface

ceramic/slag (Fig. 7.11). Although copper, lead and antimony have been identified in their metallic state, the metallic phases are clearly dominated by silver, either alloyed with a few percent of the other metals cited above or in binary dendritic systems with copper, when the latter is in relatively high concentrations (Fig. 7.12). One specific crucible shows fragments of a thick layer of copper-rich silver adhered to the inner surface of the crucible on top of a silicate slag, rich in iron and alkali oxides (Fig. 7.13). This particular vessel may be a sign of potential re-use of the crucibles, first utilised for the reducing fusion of an ore, and then for the melting of silver metal in a second separate step. Such a recycling of reaction vessels could lead to a possible contamination of the metal to be re-melted and would most likely not be considered appropriate by an assayer. However, from the huge amounts of silver lost in the various residues inferring a poor level of expertise and/or skills from the individuals having performed these operations, this re-use of a dirty vessel cannot be excluded.

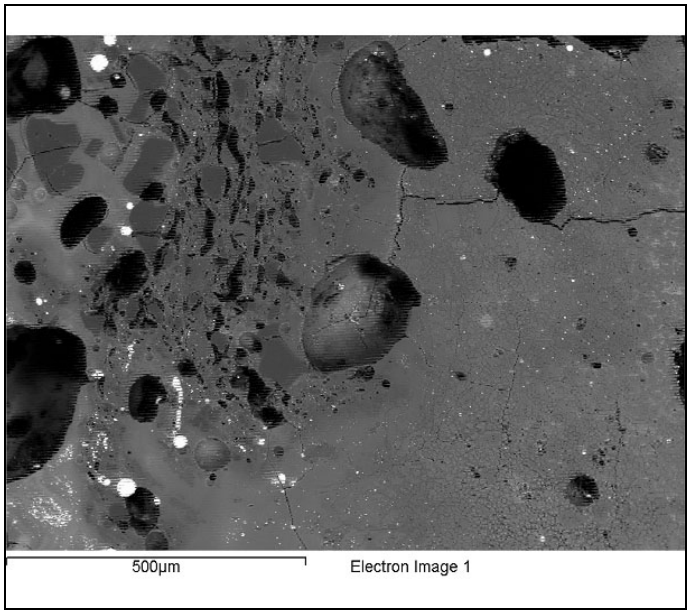


Fig. 7.11. *Large quantity of small bright silver prills trapped in the slag and at the interface between the vitrified ceramic and the slag (KA FN 164/S1, BSE, 100x).*

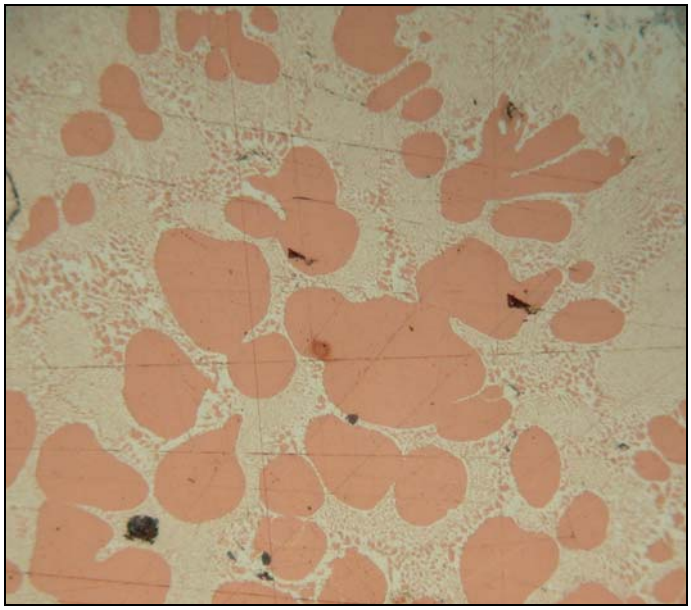


Fig. 7.12. *Dendrites of silver-rich copper (pink) with interdendritic eutectic mixture of copper- (pink) and silver-rich (white) phases (KA FN 165/S1, optical microscope, plane polarised light, 200x, long axis ~600 μm).*

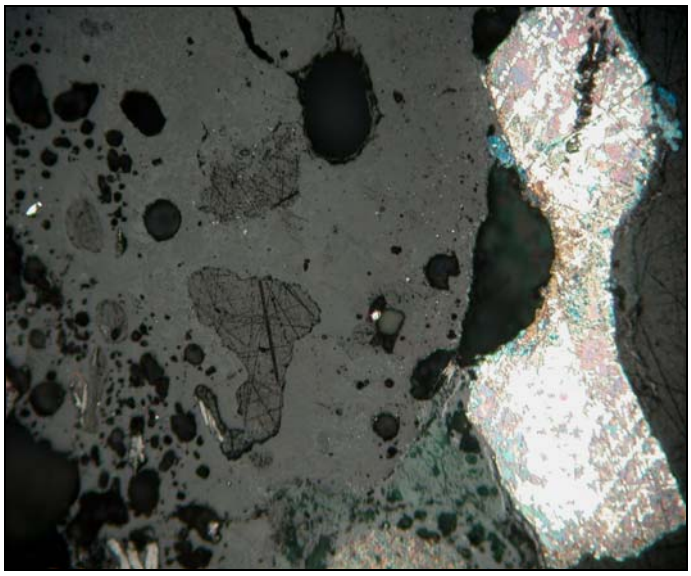


Fig. 7.13. *Bright copper-rich silver phase (right) attached to a typical iron oxide-rich silicate slag from a triangular crucible, on top of highly bloated ceramic (KA FN 167/S1, optical microscope, plane polarised light, 100x, long axis ~1.2 mm).*

From these initial data, a picture of a process similar to Oberstockall seems to emerge, namely the reducing fusion of a fahlore to extract silver from it. Several contrasting results should, however, be discussed. The first is the very irregular presence of lead in metallic phases – bullion –, and when detectable, much so in very low quantity, so that lead most certainly did not play the role of collector for silver. This is confirmed by silver being the main component of most metallic phases analysed. The second one, which could be interpreted as a consequence of the former, is the high silver loss in the various waste materials and on the surfaces of the reaction vessels. By the time this assemblage was used, fire assay had been a well-established quantitative assessment of ores and metals/alloys, and the potential

lack of awareness of metallurgical procedures and/or technical skills appears fairly puzzling, especially when compared with the level of efficiency of the earlier Oberstockstall assay and despite the latter also presenting its own technical peculiarities.

Two used scorifiers have been analysed so far and they exhibit relatively similar ceramic fabrics, with an alumina-rich clay matrix and numerous quartz grains and partially molten feldspar, resulting in an overall high potash content. The slag residues within these scorifiers show a lead silicate glass matrix, rich in alumina and in the oxides of copper and iron, soda and potash having preferentially formed feldspathoids. Despite this common characteristic, each sample has then its own distinctiveness, in a way adding to the already well-known versatility of these vessels. The first displays numerous dendrites of cuprite, clearly visible on the surface and below (Fig. 7.14-7.15), while the glass matrix of the second is in fact as rich in tin oxide (*ca.* 38 wt% SnO_2) as in lead oxide. This second slag even displays some areas of pure tin oxide, the question related to the latter being whether this phase is original cassiterite ore or if it has recrystallised from the melt. The former cuprite-rich residue has surely represented a problem during the operation, if attempting to retrieve the precious metals, since cuprite partially dissolves silver (Bayley and Eckstein 1997), and indeed *ca.* 1-2 wt% of silver have been detected in these dendrites of cuprite. As seen before, one way to avoid silver going into cuprite phases would be to increase the amount of lead added to the charge in the scorifier in order to raise the lead/copper ratio. In addition to this high loss widespread across the sample, a relatively large silver prill (*ca.* 3 wt% Cu) and a silver-copper alloy prill have been identified (Fig. 7.14). In the tin-rich specimen, several metal prills are also clearly noticeable in the slag, which can contain significant concentrations of gold (47-65 wt% Au) (Fig. 7.16). This may suggest that attempts were made to extract gold as well as silver, the two possibly parted using mineral acids, which could have been made on site as indicated by the excavated fragments of distillation apparatus.

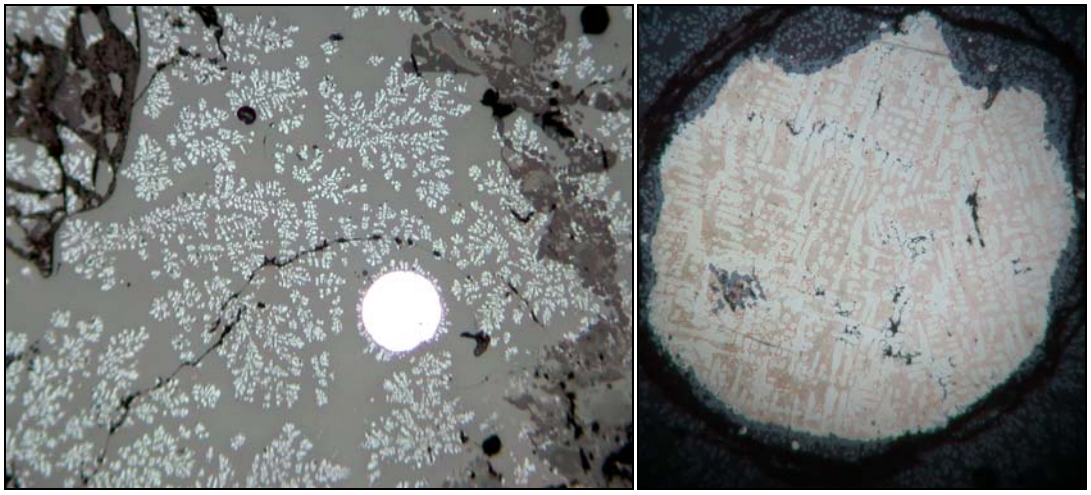


Fig. 7.14. *Numerous dendrites of cuprite in a copper oxide-rich lead silicate slag. Note the large silver prill (3 wt% Cu) (left: 100x, long axis ~1 mm). Close-up view of one of these typical prills, composed of silver-rich dendrites (white) and copper-rich interdendritic zones (pink) (right: 200x, long axis ~600 µm) (KA FN 156/S1, optical microscope, plane polarised light).*

Fig. 7.15. *Other example of the scorifier lead-silicate slag rich in dendrites of cuprite, contrasted in plane (left) and cross (right) polarised light and showing the 3D growth of these dendrites under the surface of the sample (KA FN 156/S1, optical microscope, plane polarised light, 100x, long axis ~1.5 mm).*

Fig. 7.16. *Gold-silver prill in a tin-silicate matrix on top of a lead-silicate slag with the ceramic at the bottom (KA FN 157/S1, optical microscope, plane polarised light, 100x, long axis ~1 mm).*

The high overall tin content of the latter sample could be the result of the assay of tin metal or tin ore for its silver content. This would mean that the lead detected in this slag would have been added to the charge to collect the noble metals from the raw materials. This, however, does not seem to match what has been documented for the crucible fusion so far, since the low levels of lead in crucible residues may suggest that lead was not used for this operation, however crucial this may have been – exception made of one sample displaying a crucible lead-silicate glass, though devoid of precious metals. As tin was a more expensive metal than lead, thus possibly regarded as being better, another situation may have been the use of tin as metal collector for gold instead of lead, gold being such a noble metal, perhaps "deserving" a more valuable material for its extraction. This possible substitution of lead by tin recalls the same situation documented for antimony and bismuth: all these metals were in the past regarded as species of lead and could have therefore been tested for one specific process and compared to each other. Another explanation for this high concentration of tin could be the assay of pewter, lead-tin alloy, for its silver content, which would then account for the lead contribution in the silicate slag, without any further addition of metallic lead. This sample however stands out in its levels of gold, which are higher than silver when both are alloyed together. Knowing that gold was commonly interspersed in tin ore deposits, it is therefore possible that cassiterite was assayed or simply smelted in a scorifier to recover the gold it contained. Tin ore is often found with quartz- and calcite-rich gangue, which would explain the high calcium oxide content of the slag, usually associated with tin in silicates. An explanation for the simultaneous presence of lead at this stage, which would have been the starting reaction of the two-step scorification-cupellation

method (cf. chapter 4), with an apparent absence of lead during crucible fusion requires a more comprehensive study of a larger number of vessels. Bearing in mind sixteenth-century treatises, one final interesting point to make relates to the appreciable gradient in tin concentrations, which increase when moving away from the ceramic. When assaying tin for silver, Agricola advises to melt the lead in the scorifier before placing the tin in the vessel on top of this molten lead (Hoover and Hoover 1950: 251). This would lead to the formation of a lead-silicate glass first, which would then become locally more or less enriched in tin, with areas of completely reacted tin-lead silicates and areas of pure tin metal and oxide. This is the distribution of the various tin phases, which can be seen in this sample and may point towards such a procedure. Ercker further acknowledges the use of a scorifier for the assay of tin and tin ore, rather than a crucible (Sisco and Smith 1951: 68, 279). As a general observation, in contrast to Oberstockstall, there does not seem to be any continuity between the crucible fusion and the scorification, as these operations appear to have been part of separate procedures. A clearer picture of the various processes carried out with this small assay furnace and of their relationships will need more analyses and a closer integration of the historical context of the site.

Finally, a brief account of initial analyses of cupels has been added here, based on a recent publication, which compares the results of archaeometric studies on cupels from various contexts, and more generally reflects on the potentials of this kind of research on the assessment of process efficiency in the case of cupellation (Martinón-Torres *et al. in press*). The chemical analyses of one cupel from Kapfenberg have revealed high levels of antimony (2.1 wt% Sb), nickel (0.5 wt% Ni) and silver (0.14 wt% Ag), in addition to the diagnostic matrix of lead oxide and the constituting materials of the cupel itself. The comparison between the concentrations of heavy metal oxides further emphasises the most likely mineral origin of the raw materials processed in Kapfenberg, their amounts as impurities in the body of the vessel being much higher than in the case of the cupel from the minting context of Pymont. The relative low level of technical skills of the individual cupelling silver-rich bullion in Kapfenberg is further shown by the relatively high quantities of silver detected in the cupels (Fig. 7.17). The Oberstockstall cupels plot closely around an average of *ca.* 200 ppm of silver whereas silver concentrations vary much more broadly between *ca.* 100 ppm and *ca.*

1600 ppm in the cupels from Kapfenberg with frequent high values of *ca.* 0.1-0.15 wt% of silver.

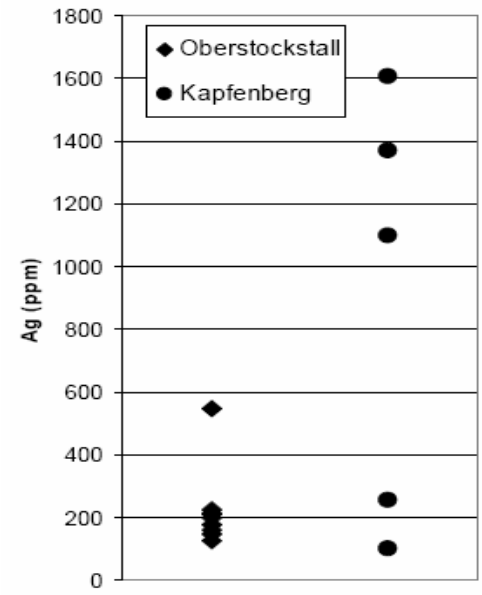


Fig. 7.17. *Silver concentration in cupels from Oberstockstall and Kapfenberg, showing the high loss occurring in the latter (after Martinón-Torres* et al. *2009).*

The concealed location of the furnace and the operations performed with it seem to suggest a level of secrecy and maybe illegality around it, which recalls the sacristy in the castle of Oberstockstall, which was most likely not an easily accessible or public place either. The overall high losses in silver in all vessels from Kapfenberg and the location of the furnace further stress the possibility of a non-professional metallurgist carrying out a variety of reactions, most likely to recover the silver – and maybe gold – from sulphidic minerals, such as fahlores, available locally. No real pattern has, however, so far emerged from these preliminary results, but it does not seem that the operations in Kapfenberg were conducted as a quantitative assessment of ores, in other words that they were processes performed within a fire assay sequence – or if it was, this fire assay was very poorly executed and of no use to any prospector or miner. Thus, there appears to be similarities in materials and procedures to some extent between the two sites of Oberstockstall and Kapfenberg, but the context of these activities seems generally different, although more research is needed to elaborate on this and get a better idea of its true nature.

On the whole, it seems that the laboratory of Oberstockstall remains a unique case study in terms of the extent and exclusivity of its assemblage and of the range of activities more or less directly connected to fire assay. Nonetheless, at a time of

continuously growing awareness and understanding of chemistry and materials, and as a result of evolution of ideas and knowledge, the second case of Kapfenberg suggests for other laboratories or similar small-scale metallurgical and chemical workplaces to have likely been set up, probably by metallurgists or chemists and non-professionals alike, with an interest in metals and/or more generally in the study of nature. Their operation could have been perfectly official through the routine fire assay of minerals for local prospectors or miners, but could also display a reverse side, which was more oriented towards fundamental research dedicated to the understanding of properties and behaviours of elements and more widely of the natural world. This is an aspect practically absent in industrial production, as will be discussed below, although fire assay of ores and alloys would certainly be a routine operation.

7.2. Industrial smelting: standardisation and optimisation of the process

On completely the opposite end of the production scale to the contemporary laboratory of Oberstockstall and the later fire assay set-up from Kapfenberg, the gold smelting site of the Angertal shows a more standardised repetition of one main procedure, seemingly with little concern with experimentation. The method employed for gold ore smelting was simply performed with the purpose of replicating a method, which was known to work efficiently and yield a valuable quantity of precious metals for trade, and the overall aim of creating a profit. Two main aspects are involved in such an industrial scale: the likely standardisation of the process reflected in the waste products, and the competence of the smelters, which can be hinted at through the precious metal contents of these waste materials. These levels of standardisation and efficiency are discussed in more detail here as they emphasise the strong disparity between the – suggested – purposes of the two sites of Oberstockstall and the Angertal.

7.2.1. Levels of standardisation and efficiency of the process

The degree of homogeneity and leanness of all the slag and matte samples analysed for this study are indicative of a fairly standardised and efficient process. The standardisation of the process is well illustrated by the silver content of the matte, which has been detected in very similar concentrations in this phase, ranging between 0.2 and 0.7 wt% Ag (Table 6.4, p. 213). This seems rather normal for an

exploitation of the scale of the Angertal during the second half of the sixteenth century. The weight of the charge was probably calculated to be roughly the same for each smelt, and hence the amount of charcoal as well, as further suggested by the relatively standard dimensions of the three furnaces, and especially furnaces 1 and 2 (Fig. 6.5, p. 195). Parameter that might change from one charge to another would have been the variation in the relative proportion of gangue components, which could have required an adjustment in the quantity of quartz to be added to the charge if it was not self-fluxing. The fairly standard composition of slag and matte however points towards a relatively good control of the proportions of raw materials in the charge, suggesting that the smelters of the Angertal did understand the proportions needed and selected the right relative amounts of iron- and silica-rich material to be smelted together and optimise the extraction of the precious metals.

The different value in the gold/silver ratio observed in one bead produced by the cupellation of archaeological lead – 0.06 compared to 0.27 for the other cupelled lead samples – may reflect the smelting of a different ore mixture, one being particularly poor in gold. This higher silver/gold ratio may otherwise be the result of a smelt, for which a relatively large quantity of matte has been added to the charge or some matte particularly rich in precious metals; the silver trapped in the matte being in much higher quantity than gold – *ca.* forty times more silver than gold – may have diluted the gold contained in the ore in an initial 3:1 ratio. This argument is nonetheless supported by only one specimen and the silver to gold ratio remains overall fairly constant. This consistency seems to further stress the standardisation of the process, and the fact that the charge may have roughly always been composed of the same reagents, added in similar proportions from one smelt to another.

However, as noted above, some gold and silver remained trapped in metal and matte inclusions in the slag, and in the matte itself. As discussed previously, precious metal concentrations in matte were around ten times smaller than the combined quantity of gold and silver actually collected by metallic lead and obtained after cupellation. At the time of main activity at the Angertal site, it has been inferred from historical sources that the ore minerals exploited could have yielded *ca.* 50-60 g/ton of gold (Gruber 2000: 175), of which 5% were estimated to go in the matte in the case of a smelt producing 10% of matte. The loss in silver being trapped in the matte layer appeared even more significant. Despite our speculative estimation, the amount of matte produced remains unknown, but if around 2 kg of bullion were

produced per 100 kg of ore with the rest being matte and slag and matte around – or perhaps at least – 10% as hypothesised, then straight discard of matte after each smelt would increase this proportion from 5% of the original quantity of gold lost to much higher absolute losses. This could be regarded as a supporting argument for the recycling of matte, which would keep these losses in precious metals to a minimum. Overall, it appears that the smelting process carried out at the Angertal site was fairly well understood, controlled and optimised for gold, but that some inevitable loss in precious metals, and mostly in silver, occurred, which may have been handled through recycling of the matte.

The recycling of matte has never been documented or suggested before from the archaeological record, although it is referred to in historical texts (Hoover and Hoover 1950:386; Smith and Gnudi 1990: 156-158). Its formation has been acknowledged in the context of silver exploitation in south-west Spain during the second and first millennia BC (Keesman 1993), for the smelting of sulphidic gold ores in Roman Portugal (Bachmann 1993) and in the Black Forest during the late medieval and early modern periods (Goldenberg 1993; 1996). It is however important to note here that these publications most likely realised the relevance of matte formation in the smelting process, but that this material was not studied in particular details as it appears quite common among the waste materials from smelting operations. This highlights the importance of the present study, in trying to understand its role within the metallurgical *chaîne opératoire* of industrial gold production.

7.2.2. Organisation of the smelting site

The three furnaces excavated at the Angertal smelting site, of probably the same size, shape, type and all arranged in a line, were operated using bellows as shown by the archaeological features around them (Fig. 6.5, p. 195). The charge smelted in these furnaces was composed of a mixture of ores from local deposits and charcoal as fuel, the former being self-fluxing if pyritic ores, iron- and quartz-rich gangue, and potentially recycled matte, were introduced in the right proportions to easily form slag. Some lead was probably added in the form of galena, which occurs as a local ore, and/or as lead metal imported to the smelting site for the specific purpose of collecting the noble metals.

The way the furnaces are aligned together raised questions regarding the organisation of the smelting operation on the site and whether these were used in parallel at the same time for the same processes, or one after the other in a sequence of three distinct but related procedures. The narrow range of elemental compositions of slag and matte from all these furnaces likely suggests that the three furnaces were operated in parallel and probably continuously. However, it is worth noting that an apparent trend can be observed for the slag recovered in the archaeological contexts directly in front of the three furnaces: there seems to be a decline in the fraction of matte trapped within the slag, with the highest amount in front of furnace 1 and the lowest in front of furnace 3 closest to the wall, which separates the working area of the site from the eastern slag heap. The decreasing abundance of matte inclusions is also reflected in the bulk slag compositions, with a decrease in iron and sulphur from furnace 1 to furnace 3 and a simultaneous increase in silica, with the highest variation occurring from furnace 1 to 2 (Table 6.2, p. 208) (Fig. 7.18). This observation, however, relies on the restricted study of a very small number of specimens, two only for each context, given that almost all the other slag specimens come from refuse areas. Such an aspect of the study may nonetheless be worth considering for future research in similar situations. The present data do not seem sufficient to support the hypothesis that the furnaces could have been run in series, the second and third furnaces perhaps processing some matte in addition to the traditional charge of ores to recover its content in precious metals. The fairly standard composition and microstructure of most of the slag except for one or two analysed samples more likely point towards a parallel run of the furnaces. The slag showing a higher matte content may merely reflect a very viscous melt for which mechanical separation of the silicate- and sulphide-rich phases was not achieved to the same level as in other smelts.

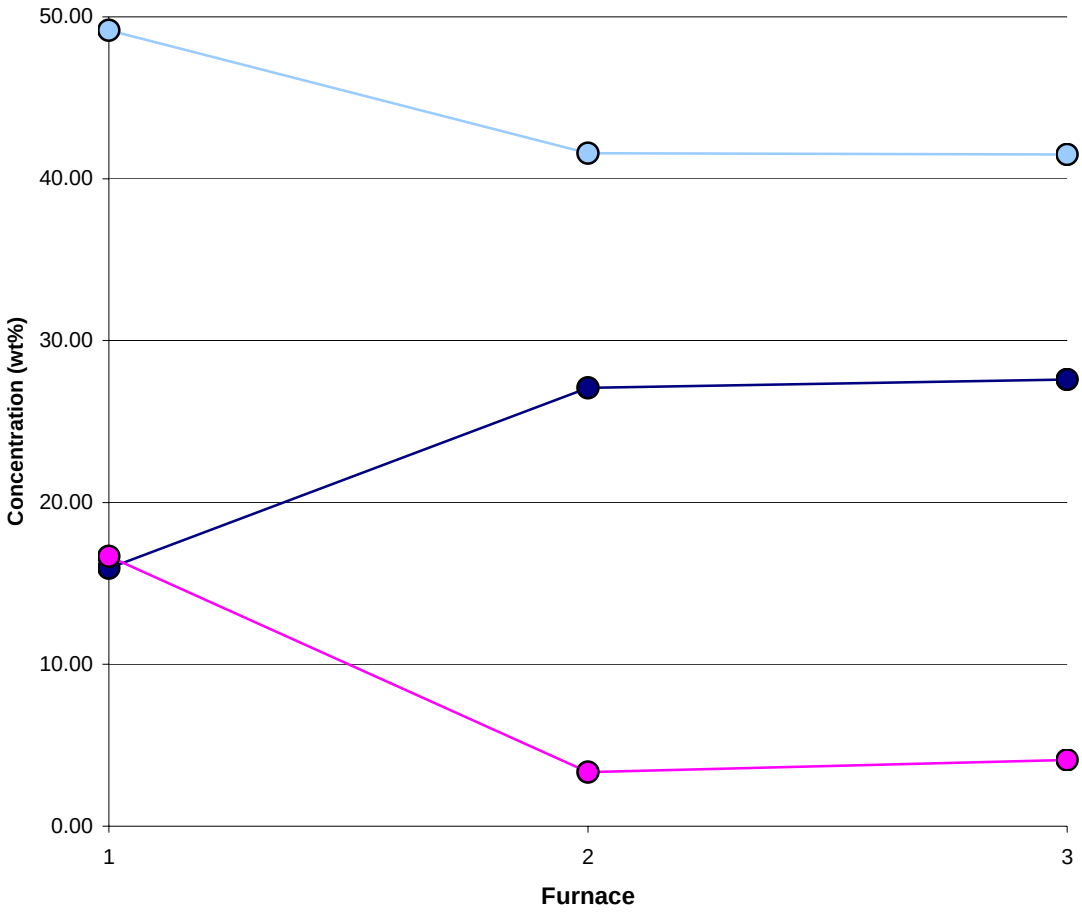


Fig. 7.18. *Diagram plotting the concentration in silica (dark blue), iron oxide (pale blue) and sulphur oxide (pink) and their respective trend from furnace 1 to furnace 3.*

If the furnaces were indeed running sequentially, with only some of them processing predominantly a relatively constant ore-matte mixture or pure matte, then one would expect to find systematic differences in their slag. The matte-processing furnaces would produce a slag with less of those oxides that go into the slag rather than the matte during the initial smelting, such as manganese oxide and barium oxide. The relatively wide range of manganese oxide concentrations in the slag, from 1.4 to 11.3 wt% (Table 6.2, p. 208) could support such a scenario of the three furnaces run in succession. However, the barium oxide values are much more consistent between all slag samples, from 165 to 465 ppm, and crucially, do not correlate with manganese oxide. Thus the current dataset is better explained by the processing of an ore with relatively variable manganese content in the gangue than by a sequential operation progressing from ore smelting to matte smelting.

The relative proportion of matte to slag produced during ore smelting remains unknown and the proportion of matte within the slag heap can only be roughly estimated. There exist several estimations of metal to slag ratios, among which one gives a bullion/slag ratio in weight slightly higher than 1:3. This ratio was initially presented by Bachmann in 1990, and adapted in a later publication to lead-silver-zinc ore smelting (Hildebrandt 1993), but does not refer to the proportion of matte to bullion or slag. Thus, an assessment of the likelihood of matte recycling as an addition to fresh ore, if based on the relative amounts of slag and matte in the slag heaps only, is virtually impossible. However, as inferred from the estimation of the proportion of silver lost in matte, the allegedly smaller amount of matte compared to slag in the total waste produced, and the frequent descriptions from sixteenth-century treatises (cf. chapters 4 and 6 and see below), matte recycling cannot be excluded and has possibly indeed taken place.

A final aspect to be considered is the location of the smelting sites, such as the one of the Angertal, which were established in the valley while mining took place in the mountains. Smelting was thus not carried out near the exploited geological deposits and the ore was transported away from the mines. This may have been because the mines were above the tree line and there was therefore no wood available to produce the large quantities of charcoal needed as fuel in the smelting operation. The ore was therefore brought to the fuel. Besides, a river or stream was necessary for the water-powered bellows, which would have been more easily found in the valley, and ore was much more conveniently brought downhill than fuel uphill, as the latter is very bulky to carry.

7.3. Comparison to contemporary texts: written descriptions vs. practice

As introduced in the beginning, another aspect of this study is the comparison between the results of this archaeological and archaeometric study and the most significant contemporary historical sources. The relationship existing between the theory and principles of the metallurgical methods described in texts and their practical counterpart inferred from the archaeological evidence allows an even deeper study of the *chaînes opératoires*, by questioning the possible choices and nature of knowledge of the individuals behind the technical sequences identified at both contemporary sites.

7.3.1. Fire assaying in sixteenth-century Oberstockstall: ignorance or technological choices?

In Oberstockstall, the dominant metallurgical sequence and the reaction vessels used seem to be in accordance with the recommendations given by Agricola and Ercker (Hoover and Hoover 1950: 226-227, 239-241; Sisco and Smith 1951: 112). Written descriptions of the procedures include a similar three-step method of crucible fusion, scorification and cupellation, with the clear addition of lead as metal collector for the crucible fusion and cupellation, and fluxes, such as the ones identified in Oberstockstall for the first reducing stage in the triangular crucible. Ercker, however, suggests to scorify both the lead bullion and the slag together (cf. chapter 4), which is clearly not what is noted in Oberstockstall, and he prefers the scorification-cupellation method (Sisco and Smith 1951: 39-40), while the main technical sequence of Oberstockstall combines crucible fusion-scorification-cupellation. However, this two-step scorification-cupellation route has been identified among the laboratory remains as a minor variant of the main operation, apparently for the processing of a different raw material, suggesting that it was known and part of the range of methods used.

At a first glance, this seems to indicate that the users of the laboratory were possibly aware of these treatises, or at least that their practice conforms with the 'typical' procedures that treatise writers would collect in their books. However, they do appear to have followed advised methods only partially, since there are two significant but closely related deviations from the standard given in books: first, the lack of roasting; and second, the occasional scorification and refining of matte, which would not be relevant if the ore(s) were first completely roasted. It clearly appears that matte was regularly produced in Oberstockstall, as shown by its presence in the archaeological assemblage. However, if metallurgical texts had been scrupulously followed, matte would most likely not have formed to this extent – only possibly as some contamination included in slag and bullion, since sulphidic minerals are advised to be roasted in a scorifier prior to reducing crucible fusion. This systematic distinction between practice and texts raises various questions regarding the intentions and motivations of the individuals working in this laboratory, since they had many scorifiers, which could have been used routinely for roasting. There is a discrepancy between what can be inferred by the archaeological material and the written sources, which makes us wonder whether the activity of this

laboratory was embedded within a professional metallurgical world – with a true awareness of contemporary recommended recipes – and whether there was a deliberate choice of methods and techniques; or whether the main procedure was discovered and achieved after a relatively long period of independent research in metallurgy and chemistry by individuals who had a very keen interest in scientific or more eclectic matters. Although there does not seem to be any precise answer to these issues, it has to be noted that, being an intentional selection of processes or not, these specific reactions, and especially the principal sequence, work relatively well in terms of efficiency. In spite of lack of initial roasting of the sulphidic raw materials, there is little silver lost in the vessels and the waste products, except maybe for the matte cakes. This would tend to show that an intermediate scorification of bullion and, when included, of matte would have worked effectively and may further emphasise the occasional refining of matte.

However, if a subsequent refining of matte by scorification was indeed happening, this would imply that the chymist of Oberstockstall was aware of the silver going into this sulphidic phase and hence getting potentially lost – even if this loss seems to have been minimal in the case of Oberstockstall –, which would result in a failure of the quantitative assay. Therefore, one wonders why the ore was not roasted in the first place to prevent this phase from being created. It is hard to believe that he would not know about this crucial step in fire assay if he was, in fact, scorifying matte. The chymist there may have wanted more from his assays than simply quantitatively assessing ores. He may have intended to test and measure the quantity of silver going into the matte phase, to get an idea of what would happen on a larger scale, as matte is actually expected to form during smelting of sulphidic ores, as seen in the case of the Angertal smelting. This assaying of matte seems to link both sites, in that the fire assay of this supposedly waste product would have been useful to the smelters in the Angertal to monitor, and possibly reduce, this loss in precious metals.

Another contrasting observation between fire assay practice and textual description regards the cooling of the products after crucible fusion. As seen in Oberstockstall, it seems that the chymist did not have one preferred standard procedure for this. He appears to have been sometimes pouring the melt in a container different from the triangular crucible, where it was then solidifying, as shown by the conical lead bullion and slag residues on spouts of several triangular

crucibles; on other occasions, he apparently left these products cool and solidify within the actual reaction vessel, i.e. the triangular crucible. The extent to which each method was followed is relatively impossible to determine, for the waste pit of the laboratory in which broken sherds would have been thrown away has not been uncovered. In contrast, according to Agricola and Ercker, the bullion-matte-slag sequence is always left to cool in the crucible, which is then broken (Hoover and Hoover 1950: 243; Sisco and Smith 1951: 112).

In addition to these variations and alternatives to the recommended scheme of reactions, the occasional scorification of matte – and perhaps of bullion and matte simultaneously – was an original innovation. The refining of matte was indeed not documented in the historical sources, most likely because it was not expected to form on the crucible scale, and it required some initiative, stressing further the potential of this laboratory in terms of researching and developing pioneering and inventive technologies, when necessary.

In summary, most of the metallurgical products analysed show clear similarities and point towards one major, uniform process, consisting of the assay of ores in order to assess their content in precious metals. On a first glance, the resulting picture would be that of a laboratory where fire assay was used as an analytical technique for commercial purposes, perhaps serving local mine prospectors. However, too many clues in this research, such as the potential use of antimony and bismuth as metal collectors instead of lead, suggest that it may have been otherwise, or at least, that routine ore assaying was not the only activity, maybe even not the main one, and that the artisans in Oberstockstall may have been conducting research experiments. The possible scorification of matte would favour such a hypothesis. This seems to have been sporadically included in the typical sequence at the site, but this procedure was never described in sixteenth-century metallurgical treatises on a small scale, or identified archaeologically in any other context. The users of this laboratory were probably familiar with fire assay techniques, but may have had their own recipes. This can be further discussed in terms of technological choices: similarly to the fact that they used both graphitic and non-graphitic crucibles, while it appeared that the refractory and technical properties of the ‘black’ crucibles were highly acknowledged, it seems that despite probably being aware of regular procedures as described in treatises, they decided at times to follow a different route.

Did they actually try the conventional way of processing sulphidic ores? If so they may have decided that their methodology was working well enough so that they did not add another step to it. An inventory of belongings of when Urban von Trenbach died included a large number of books, and historical sources suggest that the laboratory hosted travelling chymists; this may indicate an exchange of ideas and knowledge and therefore point towards further deliberate choices by the Oberstockstall chymists. Finally, this laboratory was owned by priests and located in a sacristy (cf. chapter 2), and this religious context may introduce yet another dimension to its interpretation. Were experiments simply aimed at the investigation of nature, or was there a higher ambition? Unfortunately, the present work cannot provide a definite answer to this question.

7.3.2. The Angertal smelting: a good match to recipes and methods

For the more standardised process of the Angertal gold smelting site, most of the technical features of the infrastructure and equipment used look closely similar to their contemporary descriptions in written sources. The main common characteristics are the use of blast furnaces, with the application of bellows for the air supply and in front of which forehearths were probably dug. There is an even stronger connection between Agricola's descriptions of gold ore smelting, with each of his various representations involving the use of two to three identical furnaces in parallel (Fig. 6.52, p. 239) (Hoover and Hoover 1950: 379-390). Similarly, two furnaces of the Angertal are indistinguishable, while the third one is slightly further but still in the same line, and all three furnaces have also been argued to have worked simultaneously. The formation of the three metallurgical materials lead bullion, matte, and slag documented in the Angertal finds its equivalent in the Renaissance treatises by Agricola and Biringuccio (Hoover and Hoover 1950: 381; Smith and Gnudi 1990: 154). The question of potential roasting remains unanswered from the archaeological point of view, as no evidence has been found at the site. It is however included in most texts, as a regular part of the smelting process. In the Angertal, the slag was tapped out in a forehearth in front of the furnace, together with the matte and possibly with the lead bullion. This is also a common step described in written sources – although most probably inaccurately with regards to the flowing sequence of the three layers (cf. chapter 4) –, from which we may infer that the smelters of the Angertal were following established procedures rigorously. Partial roasting of the

ore may therefore have taken place in practice, as recommended by all major sixteenth-century authors, and described in earlier sources such as Theophilus (Hawthorne and Smith 1979: 139-140). Following the same line of reasoning and despite the absence of direct archaeological evidence, this could further suggest that matte was recycled in the furnace as an additive to the ore mixture. Agricola and Pliny both explain how the slag – "scoria" – should be recycled: divided in groups of different "richnesses" and re-smelted with appropriate fluxes for Agricola, and "roasted" for Pliny, as part of the slag is still rich in lead and therefore in precious metals (Bailey 1929: 95; Hoover and Hoover 1950: 381-382). This tends to show that they may have been aware of the potential loss taking place in the various waste materials. This recycling of "rich" slag has also been suggested archaeologically (Keesman 1993; Bachmann 1993). Silver- and gold-'rich' slag may therefore have been recycled in the Angertal, this is however not possible to answer in light of the present scientific and archaeological data. Agricola does not give any precise criteria related to the partitioning of the pieces of slag between their richness in precious metals; the only explanation the smelters are given is that when slag is smelted, i.e. once it is already divided, the metal-bearing fraction will "emit much odour" unlike the group devoid of metal (Hoover and Hoover 1950: 382). Could this mean that each type of waste material would need to be fire assayed to determine its content in precious metals? This would give accurate results but seems rather like a time- and resource-consuming process. Besides, assaying slag or matte did not seem to have been part of the general canon of metallurgical practice at the time, as established in most of the Renaissance literature. However, the need to adapt to changing geological and/or economic conditions may have been an incentive to the local metallurgists for the development and application of innovative technologies in the smelting industry of sixteenth-century Austria, thus contributing to the long process of changing metallurgy from an art to a science.

Following the various discussions about matte recycling in both this chapter and the previous one (cf. chapter 6), it is only fair to say that, according to its repeated mentioning in metallurgical treatises and to the smelters apparently adhering to recipes and recommended methods, it remains a strong possibility, perhaps especially to recover relatively high quantities of silver, estimated at almost 100 g per ton of ore and representing approximately 40% of the estimated original silver content of the ore). Biringuccio slightly differentiates himself from Agricola in the

fact that he explains how lead bullion and matte should be refined together in a blast furnace with added lead (Smith and Gnudi 1990: 157). As argued in the previous chapter, this was most likely not taking place at the Angertal smelting site, since the slag is generally very consistent in composition, and attests to ore smelting rather than bullion and/or matte refining. An interesting point still related to this subject is that this refining of bullion and matte together may have been carried out on a small scale in Oberstockstall, while Biringuccio – or any of the other major Renaissance authors – does not give a description of such a procedure, since on the small scale, matte formation was prevented through roasting. The positively identified characteristics of the Angertal procedure overall match very well the techniques explained by Agricola, and his "throwing back" of crushed pieces of matte into the furnace to be re-smelted (Hoover and Hoover 1950: 386) could have been an additional step recognised as necessary and therefore routinely applied by the smelters.

The pronounced similarities between the archaeological and scientific evidence from the Angertal smelting site and the methods and equipment recorded in the contemporary texts mainly lead to the conclusion that, in an industrial context, there were probably not many options for the further optimisation of a large-scale process. The techniques, which Agricola and Biringuccio describe, may have been commonly followed in the smelting of sulphidic ores at that time. Routine industrial production most likely did not allow time, resources and money for research, especially as existing methods did work. The overall aim of the exploitation was to create a profit from the extraction of noble metals from their ores, and after a probably short experimentation period of several processes, the one combining the best efficiency, i.e. good yield and short duration, was most probably selected.

This is a clear distinction between the large scale of production and the laboratory scale, for which more apparent variations to one main sequence, and most importantly deviations from recommended procedures have been identified. This demarcation is discussed in more detail below, and contrasted to similarities and associations made between the two economic and social contexts.

7.4. Industry vs. research: different purposes, distinct behaviours

From the previous discussion in the current and earlier chapters, meaningful connections between the small- and large-scale production of gold and silver can be made, despite the usual observations of differences in man-power, quantity of ore processed and of metal produced, etc. As previously stressed, the main characteristic which would link both metallurgical sites is fire assay: it would have probably been carried out routinely on ores in the Angertal, and it seems to be the principal sequence among a variety of more questionable operations in the laboratory of Oberstockstall. There is however no archaeological evidence of sixteenth-century fire assaying in the Angertal, although a fire assay furnace was discovered at the nearby mining site of the Bockhart dated to a slightly later period, attesting to the presence of this typical activity in the mining field.

The most striking similarity between both sites is the formation of a layer of matte in between the gold- and silver-rich lead bullion and the fayalitic slag, the main difference being that this sulphide-rich waste product was expected to form during the large scale operation where its generation was most likely intentional or at least acceptable, while it was supposed to be avoided in the small-scale process (cf. chapter 4). All three layers separated mechanically by density in both the triangular crucible and the smelting furnace. The matte cakes from Oberstockstall and the platy matte produced in the Angertal were shown to be very similar in composition and microstructure, indicating similar conditions of formation.

This occurrence of a matte layer or matte cakes in both archaeological records further suggests that only partial roasting of the ore, if any, was taking place. It is possible that the smelters in the Angertal were partially roasting the ore, as the archaeological evidence seems to suggest that they adhered quite closely to the procedures advised in the documentary sources of the sixteenth century. On the contrary, the laboratory users in Oberstockstall did not appear concerned with their following of the recommendations made in these texts, and the thickness of the matte cakes found in Oberstockstall seems to indeed imply that the fahlore and other sulphidic ores were directly processed in the triangular crucibles, without any prior oxidation by roasting.

Although the smelters of the Angertal were most certainly keenly interested in the efficiency of the process while the chymists from Oberstockstall could appear

less concerned if they were experimenting rather than assaying, both processes seem to have been relatively well optimised and limited the losses in precious metals in the various layers forming in the crucible or the furnace. In the case of the Angertal procedure, the traces of gold and silver in the slag were negligible compared to the amount of these metals collected in the lead bullion (cf. chapter 6). Similarly, the skills of the chymists from Oberstockstall seem to have been sufficient to achieve a reasonably accurate assay, the main evidence being the low concentrations of silver and gold detected in the cupels (*ca.* 200 ppm Ag and *ca.* 50 ppm Au, averages of the analyses of nine cupels) (Rehren 1998). These values appear fairly constant and much lower than at the very similar site of Kapfenberg succinctly presented above (Martinón-Torres *et al. in press*), and may indeed suggest a relatively good level of expertise at Oberstockstall, as opposed to the worthless procedure carried out in Kapfenberg. The absence of speiss, which could have formed in such an antimony-rich chemical system, in both cases definitely reduced silver loss (Craddock *et al.* 1987) but it was observed that silver significantly went into the intermediate layer of matte and was therefore potentially lost if this waste product was discarded. In medieval production of precious metals, speiss was apparently known to be an undesired material, which could capture high quantities of precious metals (Goldenberg 1996; Rehren *et al.* 1999), matte however was intentionally produced in medieval copper smelting of sulphidic ores and may not have been seen as an issue, or was indeed not discarded straight away, but rather processed further.

This leads back to the issue of the recycling of matte, at Oberstockstall further submitted to scorification together with the crucible bullion, and in the Angertal most likely re-processed in the furnace as an additive to the charge. In both cases, there is no direct evidence for this, although the archaeometric study of the various waste products could direct our interpretation towards such a procedure. There is no acknowledged direct archaeological evidence for this operation either. Earlier studies have hypothesised the recycling of the lead-rich slag fraction in silver and gold smelting, i.e. slag still supposedly rich in precious metals, while the poor or lean slag was discarded (Keesman 1993; Bachmann 1993; Goldenberg 1996: 31), but none of them refer to the re-use of matte. This would seem a rather peculiar attitude, given that fire assay would quickly and certainly determine a higher loss in precious metals within the matte than in the slag. Besides, as seen above, sixteenth-century technical texts usually recommend the recycling of matte, and in the case of Agricola, of every

type of waste material. In the case of Oberstockstall, this recycling may not have been as regular as in the Angertal, as shown by the relatively wide range of iron oxide concentrations in the scorifier slag samples (*ca.* 1 to 10 wt% FeO, cf. chapter 5). The lower concentrations around *ca.* 1-2 wt% of iron oxide are probably only the sign of some contamination of the lead bullion by some matte after the reducing crucible fusion, whereas scorifier slag displaying *ca.* 5-10 wt% of iron oxide could indeed suggest that matte was scorified, possibly together with the bullion or with some additional lead to extract any gold and silver trapped. This scorification of matte may have been a consequence of having tried the scorification-cupellation assaying sequence on different ores, and noticed that this method potentially produced bullion and yielded precious metals after cupellation. If the users of the laboratory of Oberstockstal were indeed experimenting, they could have adapted a variety of methods from observations made upon more exploratory reactions. The identification of the formation and recycling/scorification of matte as intentional will however remain speculative until further archaeological evidence is found and more research on this topic carried out.

A clear difference between the two processes, on a more technical level, is the mixture of ores, which was most likely self-fluxing for smelting, while a complex recipe involving a wide variety of fluxes has been identified for the crucible fusion in Oberstockstall. The raw material was most probably indeed different – an argentiferous tetrahedrite fahlore in Oberstockstall and a wider variety of sulphidic mineral for the Angertal –, with the smelters in the Angertal having as much quartz-rich gangue available as needed. The laboratory environment was probably different and except for the contamination by gangue still attached to the ore minerals, other sources of silica-rich fluxes had to be added separately, hence the possible use of soda-lime-silica glass. In the laboratory, it would indeed make sense to use purer grade reagents, as it is much easier to ‘beneficiate’ a very small ore sample. The industrial process needed to be kept as simple as possible with as little a range of fluxes as praticable in order to render it time and cost efficient. It would not have been possible for the Angertal smelters to consider the addition of salts of various kinds, glass, iron filings and the like, as documented in Oberstockstall. Similarly, lead metal was most likely added to the ore charge in the crucibles, whereas the charge in the Angertal could have been prepared in such a way to contain enough

galena in the mixture to supply enough lead to the melt, which then in both cases acted as collector for the noble metals.

Overall, it seems that, although the two processes generated similar waste products with various levels of silver and gold potentially lost, there were clear differences in the intentions and purposes behind both activities. As shown by its historical context, the activity at the Angertal smelting site and its scale of production in the sixteenth century were clearly acknowledged and referred to in contemporary texts as a major supplier for gold and silver at that time. Oberstockstall presents the completely opposite picture of a relatively secretive and concealed laboratory located in the sacristy of a private castle and owned and potentially used by non-metallurgists by profession. No documents or written records of the activities of this laboratory have been uncovered and it does not seem likely for them to have been of public knowledge. The only historical evidence, which seems to be linked to the chemical and metallurgical operations carried out in this fire assay laboratory, is the debt left by one of the von Trenbach brothers at the local apothecary (Von Osten 1998). Such a large amount of money could have been used to potentially buy relatively vast amounts of substances and equipment for the running of a research laboratory. This is, however, pure speculation, as there are other potential explanations behind these expenses (cf. chapter 2).

In addition to the typical industry vs. research contrast, these remarkably different contexts can explain the reasons behind the technological choices made and the routes followed by both groups of individuals. The former were openly producing gold and silver from rich minerals while the latter were not only fire assaying ore but also perhaps unrealistically trying to extract “quintessences” from substances, while investigating the secrets of nature, using a rather standardised process in the first case and a wide range of interconnected small-scale reactions with a research purpose in the second situation. The combination of science, archaeology and history to research these two case studies has allowed not only the reconstruction of technical sequences, but a closer look at the actual *chaînes opératoires*, taking into account the individuals and possible intentions behind materials and actions. What could seem to have started as a simple “material-oriented” research, because of the presence of numerous unparalleled archaeological remains, revealed itself as a combination of three methodologies, which could be

seen as the way forward for present and future studies, namely material-, text- and problem-oriented (Martinón-Torres 2008). This project actually expanded to achieve more comprehensive results and interpretation, informing about individuals, their reasoning, organisation and understanding of nature in the sixteenth century, at a time when experimentation and questioning led to dramatic changes in the perception of the natural world.

Chapter 8 – Conclusions and future work

> "The man who first set gold upon the fingers was the greatest evil-doer of history, but his name is not recorded. […] The next great crime was he who first coined a gold denarius, but the matter is obscure and the originator not recorded."
>
> (Plinius 79 AD, *Historia Naturalis Liber XXXIII (8, 42)* – translated by Bailey 1932, p. 61, 81)

Gold occupies a unique position among the early metals and gold and silver have always embodied a different dimension in the metallurgy of the Old World. Whilst all other metals and alloys were produced and used for both ornamental and functional artefacts, noble metals have nearly always been considered too appealing, too valuable – too precious – for mundane practical objects. The history of gold metallurgy – and to some extent that of silver – thus opens up a range of particular aspects, for gold has been produced and found as part of most ancient material cultures in spite of the fact that, arguably, no past or modern society had a real need for it. Its particular lustre, nobility and relative rarity made it special and gave it its characteristic importance. The material peculiarities of gold and silver is also manifest in the development of techniques individual to their metallurgy, particularly refining techniques, such as cementation with salt, cupellation or acid parting, not necessary for other metals. Culturally and economically, the fascination for gold and silver also stimulated the rise of chymical activities that sought the transformation of less valuable metals into gold, which fitted the understanding of materials and approach to nature of the time for many centuries. The European Renaissance was a period of dramatic changes in the ways in which humans approached each other and the surrounding environment, and precious metals were not alien to this atmosphere. Transformations in the political and religious landscape, together with technological and philosophical developments, would lead to entirely new cosmovisions and, in the long run, to our modern configuration and understanding of the world. Given their peculiar economic, technological and cultural status, gold and silver played a central role in these transformations, and the study of the relationships between humans and noble metals thus provides a unique insight into this period, which saw, among other changes, the emergence of modern science.

The particular cultural and technological status of gold and silver appear somehow present in the unique laboratory of Oberstockstall, where it has been shown that, in addition to possible routine fire assay of noble metal-bearing ores, small-scale experimental chymical reactions were carried out, possibly in an effort to use artifice in order to understand the nature and property of natural materials. In addition to clarifying our understanding of chemical and metallurgical sixteenth-century laboratory practice, this thesis has proved relevant to the broader study of the history of science in general, and chemistry in particular, allowing a closer look at different aspects of laboratory practice during this crucial period when, for the first time, knowledge was constructed by systematically combining experiment and observation. Capitalising on the economic dimensions of noble metals, the study of the contemporary industrial gold smelting site of the Angertal enabled a contribution to our knowledge of large-scale metallurgical technologies and processes. Again, the study went beyond a mere technical approach and tried to contextualise the technology within wider economic and social aspects of the site and its role in the Gastein region, intensively exploited for precious metals at that time.

This chapter presents a brief summary of the main findings of this thesis, as well as an outline of unresolved questions and further potential that may be pursued in future research.

8.1. Metallurgical and chymical reactions in the Oberstockstall laboratory

Excavations at the sixteenth-century laboratory of Oberstockstall, in Lower Austria, unveiled a large quantity of vessels and materials, which were used for small-scale metallurgical and chymical operations. Residues from high-temperature processes were found in numerous ceramic triangular crucibles, scorifiers and ash cupels. Crucibles and scorifiers show relatively standardised shapes, with a relatively high versatility of utilisation, while the cupels are specifically designed to be used in the cupellation process. Separate lumps of bullion, matte and slag produced by these high-temperature reactions and matching the residues attached to reaction vessels, were also recovered and analysed.

The study of these remains has identified the main high-temperature sequence carried out in this laboratory as composed of three steps, namely crucible fusion, scorification and cupellation. The raw materials processed through this three-step

procedure were sulphidic ores, most likely antimony-rich fahlores, which contained precious metals. The charge for the reducing fusion in triangular crucibles was composed of the ore, to which fluxes were added, most likely in the form of iron filings, glass and salt, and lead, which acted as the collector for gold and silver. This initial step produced a top layer of slag, an intermediate matte layer and a lead-rich bullion at the bottom, separated by their specific gravity. They were either left to cool in the reaction crucible, which would then be broken to recover the products, or poured into a different receptacle to solidify, such as the conical vessels described by Ercker for parting and identified indirectly in Oberstockstall by the shape of one complete bullion cone. The slag would have then been discarded, while the bullion would have been systematically further refined by scorification, with the matte possibly occasionally so as well. The scorification of bullion or matte would produce a lead-rich bullion, which would most certainly be scorified several times to be reduced in size and well refined. The small and clean bullion produced by the last scorification, containing a high concentration of noble metals, would be finally cupelled in bone- and wood-ash cupels, resulting in a silver-gold bead, free of any impurities. This bead of noble metals may have possibly been parted with mineral acids afterwards, as suggested by the frequent finds of glass and ceramic fragments of apparatus present in the archaeological assemblage of the laboratory, and probably used for low-temperature reactions, such as distillation and sublimation.

The determination of this small-scale sequence seems to point towards a fairly consistent operation with a specific purpose: extracting gold and silver from ore samples. This technical procedure can, however, be set in two distinct contexts that would seem contraposed at first; either its purpose was the quantitative assessment of the noble metal content of ores by fire assay, perhaps to guide mining operations, or it was about the small-scale recovery of noble metals and the study of their properties and that of other materials, including the new lead-like metals antimony and bismuth, and their suitability in fire assay. The former possibility would indicate a routine, very down-to-earth process, which could have been carried out as a commercial service, while the latter would point towards a research environment, where the chymists were practically experimenting and testing minerals and the properties of materials, with a more specific focus on ‘white’ metals and an overall view on improving their knowledge and comprehension of their material world. A clarification of the intentionality behind these material remains can only be achieved

through a broader consideration of the archaeological context and our understanding of laboratory activity in the period. As argued in this thesis, the case of Oberstockstall seems to suggest that both scenarios may well have co-existed, i.e. the quantitative assay of ores with the investigation of "secrets of nature". On the one hand, most of the reaction vessels analysed seem part of this main assaying sequence that was repeated many times but, on the other hand, several samples stand out as tentative variations from it. This array of alternative processes could be interpreted as the main sign of 'scientific research', in the modern meaning of the term, happening in this laboratory. The combination of economic-driven activities with academic research is coherent with our knowledge of small-scale chymical and metallurgical activities in the Renassaince, and in this sense the Oberstockstall laboratory appears as no exception when placed in its historical context.

One reaction that suggests experimental activity includes the exploratory substitution of lead by antimony as precious metal collector in the three-step sequence, which takes place precisely in a period when the nature and properties of this metalloid were only beginning to be understood via experiments such as these. Similar, although less evident, experiments appear to have been carried out with bismuth and/or tin, which may also have been considered different types of lead. The chymists working in Oberstockstall may have wanted to study them in order to more comprehensively understand their physical and chemical properties and their different behaviours when subjected to similar chymical and metallurgical reactions. An additional peculiar operation suggested by the scientific data seems to have been the occasional scorification of matte; this reaction would have been part of the main fire assay sequence but most probably not on a regular basis, and could therefore be linked to this wider repertoire of experimental activities. The refining of matte could be further regarded as an innovation, aimed at studying the characteristics of this particular material in detail or, within the context of the fire assay of an ore, possibly at assessing quantitatively the contents in silver and gold of the matte, therefore suggesting that the chymists of Obertsockstall were aware of the loss in precious metals occurring in this phase during the crucible fusion process. Finally, in the particular case of a different ore that contained higher levels of arsenic and tin than the usual antimony-rich ore, the alternative two-step scorification-cupellation method seems to have been preferred to the main crucible fusion-scorification-cupellation sequence. This ore was clearly treated in a different way, by scorifying

the minerals directly, but possibly with fluxes similar to the crucible fusion. Incentives for experimenting seem to have included both an interest in the study of materials, and the need to adapt possibly more familiar techniques to different raw minerals. All of these aspects of the activities of the laboratory offered high-resolution information with regards to the practical choices made by the sixteenth-century chymists, which may be further contrasted and compared with theoretical discussions on natural philosophy presented in texts from the period.

A wide range of 'wet' low-temperature operations was most likely carried out in Oberstockstall, particularly distillation and sublimation, as indicated by the presence of diagnostic equipment interpreted to have been used in such reactions. These deserve a thorough scientific investigation, particularly if any remains or residues could be identified in their associated equipment, as they would nicely add to our picture of the overall reconstruction of the laboratory activities. Storage vessels and more common containers may also be relevant sources of information of the types of reagents bought and kept in this laboratory, which would for instance help in a more refined identification of the fluxes used in the high-temperature reactions carried out. The determination of a larger selection of materials would further give indications about possible choices made by the chymists in terms of 'chemicals reagents' preferentially acquired and used when various options were available.

On the whole, the study of the Oberstockstall remains gives an interesting and relatively comprehensive picture of a Renaissance laboratory where routine metallurgical and chymical operations were most likely performed at the same time as experimental reactions. In the present world, where most academic or professional enterprises lean towards extreme specialisation, such a variety of operations and intentions may appear paradoxal. In the sixteenth century, however, all of these activites could be understood as parts of the same spectrum. Importantly, all of them were coherent with the understanding of nature of that time, and even the location of the laboratory in a religious space is unlikely to be exceptional. In this sense, this laboratory can be presented as a small illustration of the changes in the perception of the world occurring during this period and, significantly, of how these changes emerged precisely through laboratory practice. It was in laboratories such as this one that modern chemistry was developed, progressively moving away from more traditional views and setting the renewed frame of mind of modern scientists.

8.2. Large-scale gold smelting in the Angertal

The region of Gastein in the Hohe Tauern, in the south of Austria, is well-known for its history of intensive and industrial exploitation of ores rich in noble metals, especially during the late medieval and early modern periods. Numerous written sources provide an insight into the geographic organisation and economic context; however, technical texts are rare, and no comprehensive archaeometallurgical study of the relevant remains has been done before. The excavation of a smelting plant of the Angertal valley, in the heart of this mining region, not only uncovered significant structural remains but also yielded a large quantity of remains and by-products such as slag and matte, potentially informative on the metallurgical process performed there. The combined archaeological and archaeometric studies of this material allowed the reconstruction of the smelting procedure . The intepretation of these data in their wider context were in part enabled thanks to the possibility of researching materials from two nearby mines, the Bockhart and the Erzwies, known from documentary sources to have been active at the time, supplying the Angertal smelting site with ores.

The archaeological features of the site show three furnaces of similar size and shape, organised in a straight line; and for which the draught was generated by bellows. Major deposits of waste material and minor heaps of similar remains scattered across the site have also been discovered. A variety of sulphidic minerals, including pyrite, galena, sphalerite, arsenopyrite, chalcopyrite and fahlore, with a gangue composed of manganese-rich iron carbonates and quartz, were found among the assemblage of metallurgical remains. These were possibly partially roasted before smelting in the three furnaces. The analytical results suggest that the three furnaces were operated in parallel for the same process and raw materials. From these data, it also appears that the galena used as an ore may have contributed enough lead to the system to collect the noble metals, not necessitating any further addition of lead as a collector for the noble metals. Sixteenth-century texts, however, recount that the transport of lead metal to be used specifically for the smelting process of noble metal-bearing ores was well organised in the Gastein region. This may suggest that, even if not chemically necessary for the reaction, lead could have been supplied to the site and added to the charge. The high-temperature smelting reaction produced lead bullion at the bottom of the furnace, with matte on top of it

and a layer of slag covering the whole melt. The three layers were likely tapped in forehearths, where they would further separate by density and settle in the same bullion-matte-slag sequence from bottom to top. The slag layer would have been skimmed off the surface of the matte when solidifying, and matte subsequently removed in a similar manner from the surface of the lead bullion. The lead bullion would then have been collected from the forehearth and kept for further cupellation. The slag was most likely discarded, as it barely contained any noble metals trapped, while matte may have been recycled, as shown by its estimated relative smaller amount in the total site waste and its non-negligible silver content. No evidence for cupellation on the smelting site has been recovered, and it is believed that the bullion was transported to urban centres such as Salzburg, where it would have been cupelled and the resulting silver-gold alloy parted.

The composition of the charge seems to have been relatively well controlled, and produced bullion, slag, and matte of fairly standardised composition. This indicates a good understanding of the process and a high level of skill of the Angertal smelters, in what probably was a technological sequence repeated innumerable times with very little modification, only seeking to maximise the yield. As argued before, the possibility of the smelters selecting very carefully the relevant pieces of ores that they knew were rich in noble metals, may further emphasise this overall high level of practical knowledge and competence of the workers. The good management of the furnace reaction allowed the smelters to conduct an optimised operation, which seems to have minimised the losses in precious metals, and especially in gold. To mitigate for the unavoidable losses in precious metals going into the matte, they most probably recycled the matte as an additive to the charges of subsequent smelts. This further suggests that the smelters may have been aware of this silver loss, which would have inevitably happened if matte were systematically forming during the reaction, as ostensibly documented at this site . The relative amount of matte discarded together with the slag is at present unknown and it is difficult to assess from the archaeological and archaeometric data whether matte was routinely re-smelted at the Angertal site. Contemporary texts regularly suggest to re-smelt matte, either on its own or as an additive to the next ore smelt. The amount of lead and silver trapped in the Angertal matte would probably have made this profitable. Fire assay, as identified in Oberstockstall and reproduced experimentally for this thesis, would have been a good means to verify quantitatively the silver content of the

matte. This was most certainly a routine procedure at the mines and could have been adapted to matte at the smelting site.

The ores from the mining districts of the Bockhart and the Erzwies have been shown to be similar to the minerals recovered in the Angertal, although these excavated pieces of ore from the smelting site may not be representative of the minerals smelted in the sixteenth century, as they appear relatively poor in noble metals and probably reflect the fraction of minerals most likely left behind. However, considering the data from the present study and the accounts from historical sources, it seems reasonable to suggest that these two mines were major ore suppliers for the Angertal. The apparent contradiction between the relatively low levels of arsenic oxide detected in the waste products from the smelting reaction, and the attested existence of a main arsenopyrite vein exploited in the sixteenth century for its precious metals, may be explained by the selective targeting of particularly rich minerals by the miners, which may have been more diverse, as suggested by the array of minerals identified in this study, even if embedded in a larger vein of arsenopyrite. Another possibility would be the specialisation of the smelting sites per type of minerals, arsenopyrite being perhaps smelted at one of the other seven known sites of this valley.

The experimental cupellation of archaeological samples of lead and matte expanded the scope of issues to be included in this thesis. Not only did it serve as an illustration of the application of a technique conspicuously documented in Oberstockstall, but it also allowed the quantification of the gold to silver ratio in the alloy produced in the Angertal, and the estimation of the gold and silver contents of the ore. The gold-silver alloy recovered from the lead bullion contained roughly 25 wt% of gold, indicating that the ores were exploited for their gold content – thus corroborating written sources. The silver associated to the gold, however, would represent a valuable by-product to be traded as well. The overall economic circumstances of the time, with the major influx of precious metals from the New World would indeed require this European mining and smelting enterprise to exploit rich raw materials to be financially sustainable.

The broader contextualisation of the technical study also showed how the Angertal site was inextricably tied into a complex and very well organised economic structure involved in the exploitation of gold- and silver-bearing ores. Several aspects of the process also proved informative regarding the skills and technological

awareness of sixteenth-century smelters. The study of this smelting site, the large-scale counterpart to the laboratory of Oberstockstall, has offered an insight into the technological choices made by miners and smelters. In stark contrast to Oberstockstall, the Angertal smelting debris indicate a highly standardised technology, with little room for routine experimentation and a major focus on exploiting a technological sequence that was known to work. However, this is not to say that smelters lacked relevant knowledge. The selection of minerals, the adjustment of furnace charges and the minimal losses altogether indicate that crucial decisions were made in practice, to maximise the yields

Future studies should incorporate remains from the other smelting plants in the Angertal, in order to verify their chronological relationships and to establish the extent to which different smelting installations were specialising on specific ores and products. More work could also be carried out to further investigate the relationships between large-scale exploitations and laboratory-scale experiments with noble metals. The mining and smelting activities documented in the Angertal probably benefited from assayers who would have guided the large-scale operations, and it is likely that the full-blown, highly efficient technology exploited in the Angertal derived from knowledge created through small-scale laboratory experiments with relevant minerals and reagents. As argued in this thesis, far from being separate worlds, laboratory and industry were two sides of the same coin, and it is hoped that this work will inspire other scholars to develop further work along similar lines.

8.3. Historical sources and scientific contextual studies of archaeological artefacts

The combination of historical, archaeological and scientific data for the study of these two sites has proved considerably useful in reaching a comprehensive reconstruction of the technological activities at each site, and also of broader matters with regards to their social and cultural contexts. Both major Renaissance technical texts and specific accounts about the history of the sites contributed to the general interpretation of the archaeological evidence, while the technological reconstructions derived from materials helped illustrate practical dimensions not always recorded in books.

The comparison between practical processes documented archaeologically, and recommended recipes from the metallurgical treatises, has shown how the chymists

in Oberstockstall seem to have been choosing different pathways to extract and assay gold- and silver-rich ores by creating their own recipes, whereas the smelters in the Angertal appear to have followed fairly accurately the advised procedures. The laboratory setting certainly allowed for more freedom in the choices of procedures and reactions, and offered more space and time to practical experimentation than in the context of industrial production where, once an efficient and optimised process had been achieved, it would most likely be kept. Combining and contrasting these three types of sources – historical, archaeological and scientific – has contributed to clarify some descriptions of processes and recipes given by sixteenth-century authors, which did not appear self-explanatory. The interpretation of the archaeometric and archaeological data informed about practical procedures and reactions, which proved a relevant tool in the partial explanation of contemporary recommended techniques and methods.

The historical accounts related to the metallurgical exploitation in the Bockhart, Erzwies, Angertal and surrounding areas, presented a larger dimension to the study by informing about the size and organisation of the overall production in the whole region, and the place and role of the particular site of the Angertal, and to some extent of the Bockhart and Erzwies mines, in the broader picture. The sixteenth-century texts about Gastein state that the sulphidic ores were intensively exploited for both gold and silver and smelted locally, which substantiates the archaeological and scientific data. These written sources also proved informative about several facts linked to the economic and social contexts, which could not be inferred or interpreted clearly from the archaeological evidence, such as the nature of the man power or the specific suppliers of the smelting site.

There is much more scope for the integration of archaeological and historical information, which cannot be obtained within the constraints of a single doctoral thesis. Given the focus of this project on technological reconstructions, the main documentary sources employed were metallurgical texts providing technical recipes together with some broader theoretical discussion. The comparison between technical reconstructions and technical texts was very fruitful. However, future work could expand the catalogue of documentary sources employed, allowing a stronger integration of these two case studies in a broader historical reconstruction. Relevant to the Oberstockstall laboratory, there is a wealth of books and documents written by chymists of the period that await focused attention. Many of them will appear

obscure and abstract at first, but they often incorporate experimental observations that may become more significant in the light of the study of the Austrian laboratory presented here. For the Angertal, although local historical sources have been consulted too, further historical and archaeological research will allow a better contextualisation of this case study in the economic map of Renaissance Europe, considering the position of this smelting site among other noble-metal producers of the period.

Following recent studies that have started to set up a more rigorous framework for the combination of history, archaeology and science, this research has tried to illustrate the usefulness of the juxtaposition of all three types of sources in the interpretation of contextual studies of technology. It is hoped that this research will have made a contribution to our understanding of early modern gold and silver extraction and may play a part in setting the ground for future studies on early modern European metallurgy and chemistry.

Appendix 1 – Precision and accuracy tests for the ED-XRF instrument using certified standards and reference materials

A1.1. Slag standards and reference materials

A1.1.1. Hawaiian basalt standard USGS BHVO-2

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	V_2O_5	Cr_2O_3	MnO	FeO	NiO	SrO	BaO	Total
	%	%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	ppm	wt%
Measure 1	2.53	4.98	16.90	49.67	0.20	0.47	10.33	2.12	0.05	0.04	0.19	12.38	133	505	158	99.93
Measure 2	2.53	4.89	16.69	49.55	0.21	0.47	10.46	2.15	0.05	0.04	0.19	12.62	144	515	157	99.93
Measure 3	2.50	4.93	16.80	49.60	0.21	0.46	10.39	2.15	0.05	0.04	0.19	12.53	140	511	151	99.92
Measure 4	2.59	4.89	16.73	49.58	0.21	0.48	10.39	2.14	0.05	0.04	0.19	12.56	134	510	158	99.92
Mean	2.54	4.92	16.78	49.60	0.21	0.47	10.39	2.14	0.05	0.04	0.19	12.52	138	510	156	99.93
Normalised mean	2.54	4.92	16.79	49.64	0.21	0.47	10.40	2.14	0.05	0.04	0.19	12.53	138	511	156	100.00
Minimum	2.50	4.89	16.69	49.55	0.20	0.46	10.33	2.12	0.05	0.04	0.19	12.38	133	505	151	
Maximum	2.59	4.98	16.90	49.67	0.21	0.48	10.46	2.15	0.05	0.04	0.19	12.62	144	515	158	
Standard deviation	0.04	0.04	0.09	0.05	b.d.l.	0.01	0.05	0.01	b.d.l.	b.d.l.	b.d.l.	0.10	5	4	3	
Coefficient of variation (%)	1	1	1	0	2	2	1	1	3	3	2	1	4	1	2	
Certified reference composition	2.22	7.23	13.50	49.90	0.27	0.52	11.40	2.73	0.05	0.04	0.17	11.07	127	473	112	99.17
Normalised	2.24	7.29	13.61	50.32	0.27	0.52	11.50	2.75	0.05	0.04	0.17	11.16	128	477	113	100.00
δ absolute	0.30	-2.37	3.18	-0.68	-0.07	-0.06	-1.10	-0.61	b.d.l.	b.d.l.	0.02	1.37	10	34	43	
δ relative (% normalised ref. comp.)	13	-32	23	-1	-24	-11	-10	-22	2	1	11	12	7	7	39	

Table A1.1. *Measured and certified values for the chemical composition of Hawaiian basalt standard USGS BHVO-2. Each measured value is the results of three consecutive runs using the "Turboquant" (Tq-0261a) method (b.d.l.: below detection limit).*

A1.1.2. Manganese nodule standard USGS NOD-1-A

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	V_2O_5	MnO	FeO
	%	%	%	%	%	%	%	%	%	%	%
Measure 1	1.42	6.11	5.74	5.79	1.32	0.72	16.00	0.66	0.19	35.58	23.03
Measure 2	1.40	5.91	5.51	5.68	1.28	0.68	15.82	0.69	0.20	35.40	22.87
Measure 3	1.11	6.03	5.80	5.82	1.30	0.69	15.84	0.70	0.20	35.19	22.74
Measure 4	1.36	6.06	5.58	5.64	1.29	0.69	15.80	0.69	0.20	35.19	22.68
Mean	1.32	6.03	5.66	5.73	1.30	0.70	15.87	0.68	0.20	35.34	22.83
Normalised mean	1.33	6.07	5.70	5.77	1.30	0.70	15.97	0.69	0.20	35.57	22.98
Minimum	1.11	5.91	5.51	5.64	1.28	0.68	15.80	0.66	0.19	35.19	22.68
Maximum	1.42	6.11	5.80	5.82	1.32	0.72	16.00	0.70	0.20	35.58	23.03
Standard deviation	0.15	0.08	0.14	0.09	0.02	0.02	0.09	0.02	0.01	0.19	0.15
Coefficient of variation (%)	11	1	2	2	1	2	1	3	3	1	1
Certified reference composition	1.00	4.76	3.87	3.81	1.40	0.60	15.40	0.53	0.14	23.90	14.04
Normalised	1.40	6.67	5.42	5.34	1.96	0.84	21.57	0.74	0.20	33.48	19.67
δ absolute	-0.07	-0.60	0.27	0.43	-0.66	-0.14	-5.61	-0.05	0.00	2.08	3.31
δ relative (% normalised ref. comp.)	-5	-9	5	8	-34	-17	-26	-7	1	6	17

Table A1.2a. *Measured and certified values for the chemical composition of manganese nodule standard USGS NOD-1-A. Each measured value is the results of three consecutive runs using the "Turboquant" (Tq-0261a) method (b.d.l.: below detection limit).*

A1.1.2. Manganese nodule standard USGS NOD-1-A (continued)

	Co_3O_4	NiO	CuO	ZnO	SrO	BaO	PbO	Total
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	%
Measure 1	4389	10866	2037	1065	1658	2505	1351	99.92
Measure 2	4478	10749	1972	1054	1635	2496	1339	99.14
Measure 3	4366	10620	1966	1039	1606	2478	1356	99.20
Measure 4	4417	10645	1968	1032	1621	2453	1330	99.18
Mean	4412	10720	1986	1048	1630	2483	1344	99.36
Normalised mean	4441	10789	1999	1054	1641	2499	1352	100.00
Minimum	4366	10620	1966	1032	1606	2453	1330	
Maximum	4478	10866	2037	1065	1658	2505	1356	
Standard deviation	48	112	34	15	22	23	12	
Coefficient of variation (%)	1	1	2	1	1	1	1	
Certified reference composition	4221	8136	1375	748	2127	1899	826	71.38
Normalised	5913	11398	1926	1047	2980	2660	1157	
δ absolute	-1473	-608	72	7	-481	-1019	195	
δ relative (% normalised ref. comp.)	-25	-5	4	1	-16	-38	17	

Table A1.2b. *Measured and certified values for the chemical composition of manganese nodule standard USGS NOD-1-A. Each measured value is the results of three consecutive runs using the "Turboquant" (Tq-0261a) method (b.d.l.: below detection limit).*

A1.1.3. Reference material "Swedish slag"

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	V_2O_5	Cr_2O_3	MnO	FeO
	%	%	%	%	%	%	%	%	%	%	%	%	%
Measure 1	1.15	0.30	7.34	21.87	0.19	0.24	0.98	1.26	0.28	0.04	0.01	3.28	62.94
Measure 2	1.05	0.28	7.14	21.50	0.19	0.23	0.97	1.28	0.28	0.04	0.02	3.31	63.56
Measure 3	0.88	0.15	7.25	21.67	0.20	0.40	0.98	1.29	0.28	0.04	0.01	3.30	63.39
Measure 4	0.84	0.25	7.18	21.64	0.20	0.37	1.00	1.28	0.28	0.04	0.01	3.31	63.45
Mean	0.98	0.25	7.23	21.67	0.19	0.31	0.98	1.28	0.28	0.04	0.01	3.30	63.33
Normalised mean	0.99	0.25	7.32	21.94	0.20	0.31	1.00	1.29	0.28	0.04	0.01	3.34	64.13
Minimum	0.84	0.15	7.14	21.50	0.19	0.23	0.97	1.26	0.28	0.04	0.01	3.28	62.94
Maximum	1.15	0.30	7.34	21.87	0.20	0.40	1.00	1.29	0.28	0.04	0.02	3.31	63.56
Standard deviation	0.14	0.06	0.09	0.15	0.01	0.09	0.01	0.01	b.d.l.	b.d.l.	b.d.l.	0.01	0.28
Coefficient of variation (%)	14	26	1	1	3	28	1	1	1	5	20	0	0
Reference composition	0.59	0.39	7.20	23.97	0.25	0.04	0.96	1.42	0.30	0.03	0.01	3.03	55.51
Normalised	0.64	0.42	7.76	25.83	0.27	0.04	1.03	1.53	0.32	0.03	0.01	3.26	59.81
δ absolute	0.36	-0.17	-0.44	-3.89	-0.07	0.27	-0.04	-0.24	-0.04	0.01	0.00	0.08	4.32
δ relative (% normalised ref. comp.)	56	-41	-6	-15	-27	629	-4	-15	-12	17	20	2	7

Table A1.3a. *Measured and certified values for the chemical composition of the reference material "Swedish slag". Each measured value is the results of three consecutive runs using the "Turboquant" (Tq-0261a) method (b.d.l.: below detection limit).*

A1.1.3. Reference material "Swedish slag" (continued)

	SrO	ZrO_2	BaO	La_2O_3	CeO_2	Total
	ppm	ppm	ppm	ppm	ppm	%
Measure 1	113	86	709	38	133	98.56
Measure 2	111	76	717	40	135	98.65
Measure 3	109	76	719	35	136	98.94
Measure 4	111	76	701	38	133	98.89
Mean	111	78	711	38	134	98.76
Normalised mean	112	79	720	38	136	100.00
Minimum	109	76	701	35	133	
Maximum	113	86	719	40	136	
Standard deviation	2	5	8	2	2	
Coefficient of variation (%)	1	6	1	5	1	
Certified reference composition	77	125	716	90	305	92.81
Normalised	83	135	771	97	329	100.00
δ absolute	29	-55	-51	-59	-193	
δ relative (% normalised ref. comp.)	35	-41	-7	-61	-59	

Table A1.3b. *Measured and certified values for the chemical composition of the reference material "Swedish slag". Each measured value is the results of three consecutive runs using the "Turboquant" (Tq-0261a) method (b.d.l.: below detection limit).*

A1.2. Ceramic standard materials

A1.2.1. Brick clay standard NBS 679

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO	Total
	%	%	%	%	%	%	%	%	%
Measure 1	0.29	1.37	24.64	55.44	2.68	0.21	0.84	13.77	99.84
Measure 2	0.08	1.27	24.16	54.69	2.64	0.22	0.84	15.38	99.84
Mean	0.18	1.32	24.40	55.06	2.66	0.21	0.84	14.58	99.84
Normalised mean	0.18	1.32	24.44	55.15	2.67	0.21	0.84	14.60	100.00
Minimum	0.08	1.27	24.16	54.69	2.64	0.21	0.84	13.77	
Maximum	0.29	1.37	24.64	55.44	2.68	0.22	0.84	15.38	
Standard deviation	0.15	0.07	0.34	0.53	0.03	0.00	0.00	1.14	
Coefficient of variation (%)	82	6	1	1	1	2	0	8	
Certified reference composition	0.18	1.25	20.80	52.07	2.93	0.23	1.28	11.64	90.38
Normalised average	0.20	1.38	23.01	57.61	3.24	0.25	1.42	12.88	100.00
δ absolute	-0.02	-0.06	1.42	-2.46	-0.58	-0.04	-0.58	1.72	
δ relative (% normalised ref. comp.)	-8	-4	6	-4	-18	-17	-41	13	

Table A1.4. *Measured and certified values for the chemical composition of the brick clay standard NBS 679. Each measured value is the results of three consecutive runs using the "Turboquant" (Tq-0261a) method (b.d.l.: below detection limit).*

A1.2.2. Burnt refractory standard NIST 67a

	Na_2O	MgO	Al_2O_3	SiO2	P_2O_5	K_2O	CaO	TiO_2	FeO	SrO	Total
	%	%	%	%	%	%	%	%	%	ppm	%
Measure 1	0.51	0.62	42.06	51.51	0.11	1.21	0.19	1.68	1.75	432	99.84
Normalised measure 1	0.51	0.62	42.12	51.58	0.11	1.22	0.19	1.68	1.75	433	100.00
Certified reference composition	0.07	0.52	38.70	54.90	0.12	1.33	0.22	2.03	1.44	400	91.68
Normalised average	0.07	0.52	38.95	55.25	0.12	1.34	0.22	2.04	1.45	403	100.00
δ absolute	0.44	0.09	3.18	-3.67	-0.01	-0.12	-0.03	-0.36	0.30	30	
δ relative (% normalised ref. comp.)	630	18	8	-7	-10	-9	-12	-18	21	8	

Table A1.5. *Measured and certified values for the chemical composition of the burnt refractory standard NIST 67a. The measured value is the results of three consecutive runs using the "Turboquant" (Tq-0261a) method (b.d.l.: below detection limit).*

A2.2.3. Firebrick standard ECRM-776-1

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	Cr_2O_3	FeO	BaO	Total
	%	%	%	%	%	%	%	%	%	%	ppm	%
Measure 1	0.37	0.41	32.54	60.41	0.06	2.61	0.28	1.38	0.02	1.57	1273	99.79
Normalised measure 1	0.37	0.41	32.60	60.53	0.06	2.62	0.28	1.38	0.02	1.57	1276	100.00
Certified reference composition	0.49	0.48	29.29	62.77	0.06	2.92	0.31	1.62	0.03	1.28	1200	99.52
Normalised average	0.49	0.48	29.48	63.17	0.06	2.94	0.31	1.63	0.03	1.29	1208	100.00
δ absolute	-0.12	-0.07	3.14	-2.62	0.00	-0.32	-0.03	-0.25	-0.01	0.28	69	
δ relative (% normalised ref. comp.)	-24	-15	11	-4	4	-11	-11	-15	-19	22	6	

Table A1.6. *Measured and certified values for the chemical composition of the firebrick standard ECRM-776-1. The measured value is the results of three consecutive runs using the "Turboquant" (Tq-0261a) method (b.d.l.: below detection limit).*

Appendix 2 – Chemical composition by SEM-EDS area analysis[8], normalised to 100%, of the glass matrices of the crucible slag from Oberstockstall

A2.1. OB 307/S2

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	FeO	ZnO	Sb_2O_3	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	4.70	0.19	9.86	45.21	0.57	0.94	3.04	7.15	13.68	6.99	1.04	6.66
Measure 2	5.50	b.d.l.	9.16	46.69	0.42	0.70	3.10	5.74	12.82	8.80	b.d.l.	7.10
Mean	**5.1**	**0.1**	**9.5**	**46.0**	**0.5**	**0.8**	**3.1**	**6.4**	**13.2**	**7.9**	**0.5**	**6.9**
Minimum	4.70	b.d.l.	9.16	45.21	0.42	0.70	3.04	5.74	12.82	6.99	b.d.l.	6.66
Maximum	5.50	0.19	9.86	46.69	0.57	0.94	3.10	7.15	13.68	8.80	1.04	7.10
Standard deviation	0.57	0.14	0.49	1.05	0.10	0.17	0.05	1.00	0.61	1.28	0.74	0.31
Coefficient of variation (%)	11	140	5	2	20	21	1	15	5	16	140	4

Table A2.1. *Chemical composition of the glass matrix of crucible slag OB 307/S2 (b.d.l.: below detection limit).*

[8] Area of analysis of 1.2 mm by 0.9 mm, at magnification 100.

A2.2. OB 345/S1

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	FeO	CuO	ZnO	SnO_2	Sb_2O_3	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%			
Measure 1	3.28	2.64	9.10	54.14	1.05	0.45	2.80	10.61	8.71	7.07	b.d.l.	0.15	b.d.l.	b.d.l.	b.d.l.
Measure 2	4.15	2.28	11.50	57.53	0.31	0.42	3.34	8.91	6.81	4.80	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Measure 3	3.21	2.91	9.32	55.92	0.97	0.53	3.04	10.14	8.56	5.22	b.d.l.	0.18	b.d.l.	b.d.l.	b.d.l.
Measure 4	5.75	1.14	17.64	60.82	0.39	0.80	6.34	1.10	3.71	1.58	0.76	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Measure 5	4.97	1.02	24.36	53.27	0.65	0.51	1.55	8.36	4.16	1.14	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Measure 6	1.96	1.89	8.44	49.46	2.01	0.85	2.59	11.59	2.19	19.02	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Measure 7*	0.99	b.d.l.	2.85	20.16	b.d.l.	b.d.l.	b.d.l.	b.d.l.	1.52	8.80	1.85	b.d.l.	1.00	14.74	48.09
Mean	**3.9**	**2.0**	**13.4**	**55.2**	**0.9**	**0.6**	**3.3**	**8.5**	**5.7**	**6.5**	**0.1**	**0.1**			
Minimum	1.96	1.02	8.44	49.46	0.31	0.42	1.55	1.10	2.19	1.14	b.d.l.	b.d.l.			
Maximum	5.75	2.91	24.36	60.82	2.01	0.85	6.34	11.59	8.71	19.02	0.76	0.18			
Standard deviation	1.36	0.78	6.35	3.88	0.62	0.18	1.62	3.79	2.72	6.55	0.31	0.09			
Coefficient of variation (%)	35	39	47	7	69	31	49	45	48	101	245	156			

** Measure 7 not included in the mean due to the very high discrepancy between this slag composition and the other six analyses.*

Table A2.2. *Chemical composition of the glass matrix of crucible slag OB 345/S1 (b.d.l.: below detection limit).*

A2.3. OB 461/S1	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	FeO	ZnO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	10.53	0.70	17.18	60.97	b.d.l.	0.65	3.38	2.66	0.38	3.27	0.28
Measure 2	12.90	1.39	19.20	50.68	b.d.l.	0.53	2.63	4.83	1.15	6.53	0.16
Measure 3	7.04	2.36	24.58	57.08	b.d.l.	0.17	3.29	1.02	1.93	2.53	b.d.l.
Measure 4	11.55	1.48	23.01	51.75	0.21	0.54	3.10	2.21	1.72	4.26	0.16
Measure 5	9.22	1.33	17.12	53.44	0.40	0.71	2.40	5.00	1.29	8.53	0.57
Measure 6	9.30	1.31	17.24	53.92	b.d.l.	0.75	2.44	5.40	1.08	7.98	0.59
Measure 7*	9.12	1.26	16.25	55.87	b.d.l.	0.87	2.55	5.01	0.93	7.50	0.65
Measure 8	9.35	1.68	16.46	54.13	b.d.l.	0.57	2.42	5.75	0.85	8.23	0.56
Measure 9	9.66	1.72	16.37	52.44	b.d.l.	0.74	2.28	5.96	1.09	9.28	0.46
Measure 10	9.39	1.46	16.20	54.25	b.d.l.	0.76	2.17	5.48	1.14	8.64	0.50
Measure 11	9.18	1.47	20.32	53.59	0.13	0.38	2.42	3.83	1.69	6.28	0.71
Measure 12	8.74	1.89	18.06	54.20	b.d.l.	0.42	2.56	4.41	1.22	8.15	0.33
Measure 13	7.46	1.10	21.26	58.51	b.d.l.	0.11	3.34	2.08	2.12	3.69	0.32
Measure 14	9.15	1.79	16.36	53.89	0.22	0.64	2.56	5.12	1.26	8.36	0.66
Measure 15	8.70	1.40	20.59	57.33	b.d.l.	0.39	3.21	2.65	1.44	4.18	0.10
Measure 16	13.02	2.01	16.11	50.25	b.d.l.	0.86	2.33	5.27	1.22	8.42	0.51
Measure 17	12.41	2.08	15.08	49.95	b.d.l.	0.63	2.29	5.78	1.30	9.82	0.67
Measure 18	11.57	2.02	16.03	49.33	b.d.l.	0.67	2.29	5.40	2.05	9.87	0.79
Measure 19	9.45	3.04	16.36	56.08	b.d.l.	0.72	2.35	4.98	1.32	5.24	0.47
Measure 20	8.42	1.91	19.25	57.50	b.d.l.	0.28	2.98	3.77	1.48	3.89	0.53
Measure 21	9.83	1.04	29.25	49.95	0.30	0.49	2.92	2.50	2.05	1.38	0.28
Measure 22	9.74	3.33	16.23	57.32	0.79	0.53	2.69	4.06	1.26	4.05	b.d.l.
Measure 23	12.92	1.11	19.78	54.23	b.d.l.	0.54	2.47	3.11	1.15	4.41	0.27
Mean	**9.9**	**1.7**	**18.6**	**54.2**	**0.1**	**0.6**	**2.6**	**4.2**	**1.4**	**6.3**	**0.4**
Minimum	7.04	0.70	15.08	49.33	b.d.l.	0.11	2.17	1.02	0.38	1.38	b.d.l.
Maximum	13.02	3.33	29.25	60.97	0.79	0.87	3.38	5.96	2.12	9.87	0.79
Standard deviation	1.69	0.62	3.39	3.07	0.19	0.20	0.38	1.42	0.42	2.55	0.23
Coefficient of variation (%)	17	36	18	6	213	36	14	34	31	41	55

Table A2.3. *Chemical composition of the glass matrix of crucible slag OB 461/S1 (b.d.l.: below detection limit).*

A2.4. OB 479/S1

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO	Sb_2O_3
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	
Measure 1	6.15	0.90	5.18	27.07	6.56	3.50	0.82	6.27	43.54
Measure 2	6.15	1.12	5.41	26.95	6.84	4.01	0.85	7.01	41.67
Measure 3	5.92	1.32	5.59	27.36	6.53	4.75	1.07	6.82	40.65
Measure 4	6.60	0.99	4.45	27.02	6.39	4.21	1.14	6.80	42.39
Measure 5	6.75	1.40	5.90	28.60	6.45	3.79	1.06	6.38	39.67
Measure 6	6.82	1.24	5.95	28.15	7.49	2.21	0.51	6.81	40.83
Measure 7	5.31	1.98	7.07	32.28	7.75	2.19	0.95	6.44	36.02
Mean	**6.2**	**1.3**	**5.6**	**28.2**	**6.9**	**3.5**	**0.9**	**6.7**	**40.7**
Minimum	5.31	0.90	4.45	26.95	6.39	2.19	0.51	6.27	36.02
Maximum	6.82	1.98	7.07	32.28	7.75	4.75	1.14	7.01	43.54
Standard deviation	0.54	0.36	0.81	1.90	0.54	0.98	0.22	0.28	2.41
Coefficient of variation (%)	9	28	14	7	8	28	24	4	6

Table A2.4. *Chemical composition of the glass matrix of crucible slag OB 479/S1 (b.d.l.: below detection limit).*

A2.5. OB 494/S1 and OB 494/S2

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	FeO	CuO	Sb_2O_3
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	5.10	1.79	12.38	37.15	1.41	0.28	6.20	11.70	0.88	15.52	1.04	6.55
Measure 2	4.27	2.22	12.85	38.21	1.68	0.30	3.77	12.93	0.40	16.44	0.10	6.83
Measure 3	4.39	1.91	12.19	37.34	1.27	0.24	3.79	13.18	0.74	17.70	0.74	6.52
Measure 4	3.67	1.77	12.32	38.60	1.55	0.83	3.96	12.01	0.59	16.80	b.d.l.	7.90
Measure 5	4.02	2.20	12.99	39.34	0.94	b.d.l.	4.25	14.01	0.27	15.95	b.d.l.	6.03
Measure 6	4.36	2.22	12.90	41.54	1.25	b.d.l.	3.91	14.11	0.49	15.98	0.42	2.82
Measure 7	4.34	2.31	13.21	41.39	1.00	0.38	3.96	14.84	0.63	15.81	0.55	1.57
Measure 8	4.50	2.35	12.77	41.65	1.60	b.d.l.	4.05	14.47	0.60	15.40	0.34	2.27
Measure 9	3.67	2.26	12.46	41.21	1.00	0.16	4.20	12.59	0.17	14.73	0.45	7.10
Measure 10	3.99	2.05	11.77	36.53	1.58	b.d.l.	3.58	13.58	0.57	19.08	0.25	7.01
Measure 11	4.75	1.59	14.09	38.18	1.47	0.90	4.81	10.42	0.46	16.51	b.d.l.	6.82
Mean	**4.2**	**2.1**	**12.6**	**39.3**	**1.3**	**0.2**	**4.2**	**13.3**	**0.5**	**16.3**	**0.4**	**5.5**
Minimum	3.67	1.59	11.77	36.53	0.94	b.d.l.	3.58	10.42	0.17	14.73	b.d.l.	1.57
Maximum	5.10	2.35	14.09	41.65	1.68	0.90	6.20	14.84	0.88	19.08	1.04	7.90
Standard deviation	0.43	0.26	0.61	1.94	0.27	0.32	0.73	1.33	0.20	1.20	0.34	2.22
Coefficient of variation (%)	10	12	5	5	20	146	18	10	38	7	86	41

Table A2.5. *Chemical composition of the glass matrix of crucible slag OB 494/S1 (measures 1 to 8) and OB 494/S2 (measures 9 to 11) (b.d.l.: below detection limit).*

A2.6. OB 498/S1

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	FeO	ZnO	Sb_2O_3
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	8.09	1.18	11.97	41.36	0.39	1.23	1.69	7.24	0.06	16.48	b.d.l.	10.31
Measure 2	4.79	1.18	12.84	42.24	0.38	1.45	1.83	7.26	0.22	17.49	0.28	10.05
Measure 3	6.68	1.04	14.07	38.34	0.56	1.15	2.09	6.20	0.39	20.14	b.d.l.	9.36
Measure 4	8.40	1.22	11.99	39.71	0.44	1.31	1.64	7.72	0.13	15.25	0.00	12.19
Measure 5	8.19	1.24	12.95	38.16	0.45	1.69	1.82	5.33	0.23	20.31	0.11	9.52
Measure 6	7.76	0.64	12.63	37.83	0.44	2.99	1.09	6.41	0.27	22.28	0.26	7.39
Mean	**7.3**	**1.1**	**12.7**	**39.6**	**0.4**	**1.6**	**1.7**	**6.7**	**0.2**	**18.7**	**0.1**	**9.8**
Minimum	4.79	0.64	11.97	37.83	0.38	1.15	1.09	5.33	0.06	15.25	b.d.l.	7.39
Maximum	8.40	1.24	14.07	42.24	0.56	2.99	2.09	7.72	0.39	22.28	0.28	12.19
Standard deviation	1.38	0.23	0.77	1.84	0.06	0.69	0.33	0.88	0.11	2.68	0.13	1.56
Coefficient of variation (%)	19	21	6	5	15	42	20	13	52	14	122	16

Table A2.6. *Chemical composition of the glass matrix of crucible slag OB 498/S1 (b.d.l.: below detection limit).*

A2.7. OB 509/S1

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	FeO	ZnO	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	4.29	1.71	5.74	36.74	0.32	3.06	5.50	0.37	8.86	0.29	33.14
Measure 2	3.82	1.77	5.52	34.90	0.26	2.43	7.74	0.44	8.32	0.00	34.80
Measure 3	4.11	2.03	5.32	35.30	0.38	2.49	7.23	0.35	6.93	0.29	35.58
Measure 4	4.31	1.33	5.43	37.27	0.16	2.98	5.93	0.52	6.92	0.00	35.16
Mean	**4.1**	**1.7**	**5.5**	**36.1**	**0.3**	**2.7**	**6.6**	**0.4**	**7.8**	**0.1**	**34.7**
Minimum	3.82	1.33	5.32	34.90	0.16	2.43	5.50	0.35	6.92	0.00	33.14
Maximum	4.31	2.03	5.74	37.27	0.38	3.06	7.74	0.52	8.86	0.29	35.58
Standard deviation	0.22	0.29	0.18	1.13	0.09	0.33	1.06	0.08	0.99	0.17	1.07
Coefficient of variation (%)	5	17	3	3	33	12	16	18	13	115	3

Table A2.7. *Chemical composition of the glass matrix of crucible slag OB 509/S1 (b.d.l.: below detection limit).*

A2.8. OB N001/S1 and OB N001/S2

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	FeO	CuO	ZnO	Sb_2O_3	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	0.16	2.51	16.51	51.90	0.37	b.d.l.	7.10	4.58	10.74	2.61	0.44	2.80	0.29
Measure 2	b.d.l.	1.49	1.51	39.48	0.88	0.27	2.38	6.72	18.31	6.52	0.19	18.73	3.30
Measure 3	b.d.l.	2.21	15.91	55.05	b.d.l.	0.34	7.61	4.44	11.30	1.99	0.28	0.55	0.32
Measure 4	b.d.l.	2.24	b.d.l.	39.39	1.04	0.49	2.55	6.92	17.61	5.49	b.d.l.	21.26	2.66
Measure 5	b.d.l.	2.85	18.11	49.33	0.22	b.d.l.	7.14	4.87	11.40	2.93	0.32	2.37	0.45
Measure 6	0.22	1.77	10.44	54.82	0.42	0.27	8.60	3.69	12.28	3.52	b.d.l.	3.37	0.60
Measure 7	0.31	2.80	2.07	37.74	0.94	0.40	2.05	9.77	16.81	4.45	b.d.l.	19.74	2.75
Measure 8	b.d.l.	2.33	2.07	40.07	0.97	1.06	2.24	7.08	16.69	6.14	b.d.l.	18.49	2.71
Measure 9	0.40	2.15	1.78	43.39	1.59	1.53	2.19	6.88	15.09	4.50	b.d.l.	20.26	b.d.l.
Measure 10	b.d.l.	2.54	7.48	21.78	1.60	1.97	4.43	20.20	15.39	3.31	b.d.l.	15.14	4.45
Measure 11	b.d.l.	1.63	0.93	16.26	4.41	0.56	1.89	6.92	18.92	5.49	b.d.l.	30.86	12.14
Measure 12	0.27	1.95	6.36	31.48	0.78	b.d.l.	3.86	17.54	14.17	3.32	1.01	15.36	4.05
Measure 13	0.29	1.85	1.26	29.24	2.02	b.d.l.	1.92	8.26	21.42	6.58	0.70	23.57	2.61
Measure 14	b.d.l.	1.70	3.37	27.35	1.07	b.d.l.	2.58	16.93	15.46	4.10	0.26	18.56	8.61
Mean	**0.1**	**2.1**	**6.3**	**38.4**	**1.2**	**0.5**	**4.0**	**8.9**	**15.4**	**4.4**	**0.2**	**15.3**	**3.3**
Minimum	b.d.l.	1.49	b.d.l.	16.26	b.d.l.	b.d.l.	1.89	3.69	10.74	1.99	b.d.l.	0.55	b.d.l.
Maximum	0.40	2.85	18.11	55.05	4.41	1.97	8.60	20.20	21.42	6.58	1.01	30.86	12.14
Standard deviation	0.15	0.43	6.42	12.09	1.09	0.61	2.47	5.33	3.18	1.49	0.31	9.29	345
Coefficient of variation (%)	128	20	102	31	93	125	61	60	21	34	136	61	106

Table A2.8. *Chemical composition of the glass matrix of crucible slag OB N001/S1 (measures 10 to 14) and OB N001/S2 (measures 1 to 9) (b.d.l.: below detection limit).*

Appendix 3 – Chemical composition by SEM-EDS area analysis[9], normalised to 100%, of the glass matrices of the scorifier slag from Oberstockstall

A3.1. OB 268/S1

	Al_2O_3	SiO_2	K_2O	CaO	FeO	CuO	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	4.71	16.92	0.53	0.88	5.77	0.82	70.38
Measure 2	8.48	23.69	0.97	0.88	4.34	b.d.l.	61.65
Measure 3	4.34	17.30	0.38	1.11	5.73	0.89	70.25
Measure 4	2.37	10.74	b.d.l.	0.89	5.78	1.40	78.83
Mean	**5.0**	**17.2**	**0.5**	**0.9**	**5.4**	**0.8**	**70.3**
Minimum	2.37	10.74	b.d.l.	0.88	4.34	b.d.l.	61.7
Maximum	8.48	23.69	0.97	1.11	5.78	1.40	78.8
Standard deviation	2.55	5.29	0.40	0.11	0.71	0.58	7.0
Coefficient of variation (%)	51	31	85	12	13	74	10.0

Table A3.1. *Chemical composition of the glass matrix of scorifier slag OB 268/S1.*

[9] Area of analysis of 1.2 mm by 0.9 mm, at magnification 100.

A3.2. OB 269/S1

	Al_2O_3	SiO_2	PbO
	wt%	wt%	wt%
Measure 1	2.31	8.17	89.52
Measure 2	2.78	8.01	89.21
Measure 3	2.35	8.17	89.48
Measure 4	2.39	8.36	89.25
Mean	**2.5**	**8.2**	**89.4**
Minimum	2.31	8.01	89.21
Maximum	2.78	8.36	89.52
Standard deviation	0.22	0.14	0.16
Coefficient of variation (%)	9	2	0

Table A3.2. *Chemical composition of the glass matrix of scorifier slag OB 269/S1.*

A3.3. OB 270/S1

	MgO	Al_2O_3	SiO_2	CaO	FeO	CuO	As_2O_3	PbO
	wt%	wt%	wt%	wt%	wt%	wt%		wt%
Measure 1	b.d.l.	2.97	12.54	b.d.l.	5.55	1.86	b.d.l.	77.08
Measure 2	b.d.l.	2.68	12.50	b.d.l.	4.04	1.70	b.d.l.	79.10
Measure 3	b.d.l.	2.49	10.01	b.d.l.	11.97	b.d.l.	b.d.l.	75.53
Measure 4	b.d.l.	2.19	7.57	b.d.l.	17.23	2.24	b.d.l.	70.77
Measure 5	1.02	2.44	8.92	b.d.l.	13.82	2.56	b.d.l.	71.23
Measure 6	1.19	1.66	7.29	0.77	21.76	3.89	b.d.l.	63.34
Measure 7	b.d.l.	3.09	10.74	b.d.l.	10.35	b.d.l.	b.d.l.	75.83
Measure 8	b.d.l.	3.16	11.03	b.d.l.	4.83	b.d.l.	b.d.l.	80.98
Measure 9	1.25	3.29	9.29	b.d.l.	16.75	b.d.l.	b.d.l.	69.42
Measure 10	b.d.l.	2.13	10.01	b.d.l.	3.82	1.30	b.d.l.	82.71
Measure 11	b.d.l.	0.32	5.47	b.d.l.	6.58	2.76	1.10	83.66
Mean	**0.3**	**2.4**	**9.6**	**0.1**	**10.6**	**1.5**	**0.1**	**75.4**
Minimum	b.d.l.	0.32	5.47	b.d.l.	3.82	b.d.l.	b.d.l.	63.34
Maximum	1.25	3.29	12.54	0.77	21.76	3.89	1.10	83.66
Standard deviation	0.54	0.85	2.19	0.23	6.19	1.35	0.33	6.24
Coefficient of variation (%)	172	35	23	332	58	91	332	8

Table A3.3. *Chemical composition of the glass matrix of scorifier slag OB 270/S1.*

A3.4. OB 271/S1

	MgO	Al_2O_3	SiO_2	FeO	Sb_2O_3	PbO
	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	0.39	0.15	1.65	2.41	84.22	11.21
Measure 2	b.d.l.	1.00	2.87	0.58	91.45	4.10
Mean	**0.2**	**0.6**	**2.3**	**1.5**	**87.8**	**7.7**
Minimum	b.d.l.	0.15	1.65	0.58	84.22	4.10
Maximum	0.39	1.00	2.87	2.41	91.45	11.21
Standard deviation	0.28	0.60	0.86	1.29	5.11	5.03
Coefficient of variation (%)	141	104	38	87	6	66

Table A3.4. *Chemical composition of the glass matrix of scorifier slag OB 271/S1.*

A3.5. OB 273/S1

	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO	CuO	As_2O_3	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	5.80	22.83	0.65	1.16	0.17	1.02	b.d.l.	1.44	66.94
Measure 2	7.72	24.71	0.30	0.83	0.69	1.71	b.d.l.	1.61	62.47
Measure 3	5.74	20.04	0.55	0.24	0.46	0.98	1.48	b.d.l.	70.50
Measure 4	5.80	20.78	0.43	0.42	0.52	0.90	1.17	0.31	69.67
Measure 5	5.94	20.90	0.38	0.18	0.40	0.84	1.37	0.29	69.71
Measure 6	5.21	18.45	0.44	0.48	0.50	0.96	1.06	0.43	72.46
Measure 7	5.18	18.28	0.48	0.24	b.d.l.	0.68	0.66	b.d.l.	74.46
Mean	**5.9**	**20.9**	**0.5**	**0.5**	**0.4**	**1.0**	**0.8**	**0.6**	**69.5**
Minimum	5.18	18.28	0.30	0.18	b.d.l.	0.68	b.d.l.	b.d.l.	62.47
Maximum	7.72	24.71	0.65	1.16	0.69	1.71	1.48	1.61	74.46
Standard deviation	0.85	2.30	0.11	0.36	0.23	0.33	0.62	0.66	3.88
Coefficient of variation (%)	14	11	25	71	59	32	75	114	6

Table A3.5. *Chemical composition of the glass matrix of scorifier slag OB 273/S1.*

A3.6. OB 274/S1

	Al_2O_3	SiO_2	K_2O	CuO	PbO
	wt%	wt%	wt%	wt%	wt%
Measure 1	3.17	10.98	0.51	0.41	84.92
Measure 2	3.28	11.24	0.49	b.d.l.	85.00
Mean	**3.2**	**11.1**	**0.5**	**0.2**	**85.0**
Minimum	3.17	10.98	0.49	b.d.l.	84.92
Maximum	3.28	11.24	0.51	0.41	85.00
Standard deviation	0.08	0.18	0.01	0.29	0.06
Coefficient of variation (%)	2	2	3	141	0

Table A3.6. *Chemical composition of the glass matrix of scorifier slag OB 274/S1.*

A3.7. OB 276/S1

	Al_2O_3	SiO_2	CaO	FeO	PbO
	wt%	wt%	wt%	wt%	wt%
Measure 1	4.59	15.28	b.d.l.	1.75	78.38
Measure 2	7.45	22.25	b.d.l.	5.76	64.55
Measure 3	5.94	26.14	b.d.l.	4.05	63.87
Measure 4	4.33	13.96	b.d.l.	1.48	80.23
Measure 5	2.93	10.19	b.d.l.	0.87	86.00
Measure 6	3.70	13.31	b.d.l.	1.39	81.60
Measure 7	4.26	17.00	b.d.l.	1.30	77.44
Measure 8	4.76	15.78	0.75	1.17	77.54
Measure 9	4.94	14.90	b.d.l.	1.81	78.35
Mean	**4.8**	**16.5**	**0.1**	**2.2**	**76.4**
Minimum	2.93	10.19	b.d.l.	0.87	63.87
Maximum	7.45	26.14	0.75	5.76	86.00
Standard deviation	1.30	4.84	0.25	1.63	7.43
Coefficient of variation (%)	27	29	300	75	10

Table A3.7. *Chemical composition of the glass matrix of scorifier slag OB 276/S1.*

A3.8. OB 277/S

	Al_2O_3	SiO_2	FeO	CuO	PbO
	wt%	wt%	wt%	wt%	wt%
Measure 1	3.14	12.75	1.59	3.21	79.31
Measure 2	5.01	19.35	2.30	3.16	70.18
Measure 3	5.15	18.56	2.26	2.66	71.37
Mean	**4.4**	**16.9**	**2.1**	**3.0**	**73.6**
Minimum	3.14	12.75	1.59	2.66	70.18
Maximum	5.15	19.35	2.30	3.21	79.31
Standard deviation	1.12	3.60	0.40	0.30	4.96
Coefficient of variation (%)	25	21	19	10	7

Table A3.8. *Chemical composition of the glass matrix of scorifier slag OB 277/S1.*

A3.9. OB 279/S1

	Al_2O_3	SiO_2	K_2O	CaO	FeO	As_2O_3	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	4.00	10.37	1.38	b.d.l.	2.55	6.42	75.27
Measure 2	4.38	11.52	1.79	b.d.l.	2.68	6.10	73.54
Measure 3	3.15	10.68	b.d.l.	b.d.l.	3.99	4.19	77.99
Measure 4	4.11	12.27	b.d.l.	b.d.l.	3.58	3.48	76.56
Measure 5	b.d.l.	6.82	b.d.l.	1.58	b.d.l.	12.98	78.61
Measure 6	3.82	9.54	2.63	1.40	b.d.l.	11.06	71.55
Measure 7	1.88	8.57	b.d.l.	0.79	1.52	9.67	77.56
Measure 8	3.73	11.5	b.d.l.	b.d.l.	2.21	7.11	75.45
Measure 9	1.62	8.02	b.d.l.	1.36	0.77	11.05	77.18
Measure 10	2.14	9.24	b.d.l.	1.25	0.84	9.99	76.54
Measure 11	1.57	8.51	b.d.l.	1.00	0.67	11.15	77.10
Mean	**2.8**	**9.7**	**0.5**	**0.7**	**1.7**	**8.5**	**76.1**
Minimum	0.00	6.82	0.00	0.00	0.00	3.48	71.55
Maximum	4.38	12.27	2.63	1.58	3.99	12.98	78.61
Standard deviation	1.40	1.69	0.95	0.67	1.39	3.15	2.07
Coefficient of variation (%)	51	17	180	100	81	37	3

Table A3.9. *Chemical composition of the glass matrix of scorifier slag OB 279/S1.*

A3.10. OB 281/S1

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	FeO	CuO	ZnO	As_2O_3	Sb_2O_3	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	b.d.l.	b.d.l.	3.40	11.50	b.d.l.	b.d.l.	4.93	3.68	b.d.l.	b.d.l.	6.03	70.46
Measure 2	b.d.l.	b.d.l.	3.67	12.63	b.d.l.	b.d.l.	5.77	1.74	b.d.l.	1.06	6.58	68.55
Measure 3	b.d.l.	b.d.l.	2.53	8.97	b.d.l.	b.d.l.	4.01	1.08	b.d.l.	b.d.l.	5.65	77.76
Measure 4*	7.00	0.60	6.70	34.10	1.30	2.60	10.30	0.80	0.50	1.60	5.80	28.20
Mean			**3.2**	**11.0**			**4.9**	**2.2**		**0.4**	**6.1**	**72.3**
Minimum			2.53	8.97			4.01	1.08		b.d.l.	5.65	68.55
Maximum			3.67	12.63			5.77	3.68		1.06	6.58	77.76
Standard deviation			0.60	1.87			0.88	1.35		0.61	0.47	4.86
Coefficient of variation (%)			19	17			18	62		173	8	7

** Measure 4 not included in the mean due to the very high discrepancy between this slag composition and the other three analyses.*

Table A3.10. *Chemical composition of the glass matrix of scorifier slag OB 281/S1.*

A3.11. OB 284/S1

	Al_2O_3	SiO_2	CaO	FeO	As_2O_3	Sb_2O_3	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	1.77	5.04	3.66	5.37	1.04	76.36	6.76
Measure 2	1.89	6.54	4.19	5.87	1.20	74.41	5.90
Measure 3	1.64	6.18	b.d.l.	5.73	b.d.l.	76.64	9.81
Measure 4	2.38	6.32	b.d.l.	5.55	1.26	65.71	18.78
Measure 5	2.26	7.91	b.d.l.	4.12	2.91	49.23	33.57
Measure 6	1.98	6.12	b.d.l.	5.23	1.74	50.47	34.07
Mean	**2.0**	**6.4**	**1.3**	**5.3**	**1.4**	**65.6**	**18.1**
Minimum	1.64	5.04	b.d.l.	4.12	b.d.l.	49.23	5.90
Maximum	2.38	7.91	4.19	5.87	2.91	76.64	34.07
Standard deviation	0.28	0.92	2.03	0.63	0.95	12.74	12.97
Coefficient of variation (%)	14	15	155	12	70	19	71

Table A3.11. *Chemical composition of the glass matrix of scorifier slag OB 284/S1.*

A3.12. OB N006/S1

	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	FeO	CuO	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	0.89	5.20	13.60	0.52	1.84	b.d.l.	2.18	5.02	70.75
Measure 2	1.03	6.40	16.20	1.10	1.77	0.73	2.03	4.65	66.08
Measure 3	0.86	4.21	13.12	b.d.l.	1.68	b.d.l.	1.91	5.07	73.16
Measure 4	1.27	4.76	14.43	b.d.l.	2.38	b.d.l.	2.04	3.11	72.01
Measure 5	b.d.l.	4.35	13.55	b.d.l.	1.60	b.d.l.	2.11	4.05	74.34
Measure 6	0.89	3.93	12.75	b.d.l.	2.38	b.d.l.	1.84	4.10	74.11
Measure 7	1.18	3.91	12.98	b.d.l.	5.25	b.d.l.	1.74	3.29	71.66
Measure 8	1.08	4.25	13.35	b.d.l.	2.02	b.d.l.	1.98	4.04	73.28
Measure 9	1.00	4.45	13.46	b.d.l.	2.10	b.d.l.	2.03	4.94	72.01
Measure 10	0.96	4.74	14.54	0.51	2.23	b.d.l.	2.12	2.92	71.98
Mean	**0.9**	**4.6**	**13.8**	**0.2**	**2.3**	**0.1**	**2.0**	**4.1**	**71.9**
Minimum	b.d.l.	3.91	12.75	b.d.l.	1.60	b.d.l.	1.74	2.92	66.08
Maximum	1.27	6.40	16.20	1.10	5.25	0.73	2.18	5.07	74.34
Standard deviation	0.35	0.74	1.02	0.38	1.06	0.23	0.13	0.80	2.35
Coefficient of variation (%)	38	16	7	178	46	316	7	20	3

Table A3.12. *Chemical composition of the glass matrix of scorifier slag OB N006/S1.*

Appendix 4 – Chemical composition by XRF analysis of specimens of ore, matte and slag from the Angertal.

A4.1. Ore specimens from the Angertal smelting site

	Mg	Al	Si	S	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Ag	Cd	Sb	Ba	Pb	Total
	wt%	wt%	wt%	wt%	ppm	ppm	wt%	wt%	wt%	ppm	ppm	wt%	wt%	ppm	ppm	ppm	ppm	wt%	wt%
AN 32/2/S1	7.62	1.99	27.61	4.49	235	240	b.d.l.	31.07	0.06	b.d.l.	139	b.d.l.	27.07	34	1	74	37	0.02	100.00
AN 58/1/S1	b.d.l.	b.d.l.	b.d.l.	9.04	33	b.d.l.	2.62	10.95	b.d.l.	110	7800	8.21	0.20	1470	345	797	b.d.l.	67.92	100.00
AN 60/1/S1	0.15	0.75	39.45	6.16	25	235	2.73	23.66	0.04	31	2639	12.78	0.24	527	769	98	b.d.l.	13.58	99.97
AN 64/2/S1	b.d.l.	b.d.l.	1.04	10.29	57	b.d.l.	0.45	4.36	0.01	25	7500	43.56	b.d.l.	594	2014	218	9	39.24	100.00
AN 7/1/S1	2.23	0.56	22.99	13.90	233	280	b.d.l.	44.43	0.04	b.d.l.	119	b.d.l.	15.51	31	1	78	21	0.10	99.84
AN 90/1/S2	0.28	0.26	22.07	15.55	219	289	b.d.l.	46.49	0.03	b.d.l.	136	b.d.l.	14.73	111	b.d.l.	79	13	0.36	99.85
Average	**1.7**	**0.6**	**18.9**	**9.9**	**133**	**174**	**0.97**	**26.8**	**0.03**	**27**	**3055**	**10.8**	**9.6**	**461**	**522**	**224**	**13**	**20.2**	**99.9**
Minimum	b.d.l.	b.d.l.	b.d.l.	4.49	25	b.d.l.	b.d.l.	4.36	b.d.l.	b.d.l.	119	b.d.l.	b.d.l.	31	b.d.l.	74	b.d.l.	0.02	
Maximum	7.62	1.99	39.45	15.55	235	289	2.73	46.49	0.06	109	7800	43.56	27.07	1470	2014	797	37	67.92	
Standard deviation	3.02	0.75	15.50	4.29	105	137	1.33	17.21	0.02	42	3690	16.94	11.27	553	792	286	14	27.89	
Coefficient of variation (%)	176	125	82	43	79	78	138	64	71	154	121	157	117	120	152	128	104	138	

Table A4.1. *Measurements of the chemical composition of pieces of ore from the Angertal smelting site. Each measured value is the results of three consecutive runs using the "Alloy" method. The detected values for cobalt reflect some contamination from the preparation process of the pressed pellets (b.d.l.: below detection limit).*

A4.2. Ore specimens from the Bockhart mine

	Mg	Al	Si	S	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Ag	Cd	Sb	Ba	Pb	Total
	wt%	wt%	wt%	wt%	ppm	ppm	wt%	wt%	ppm	ppm	wt%	wt%	wt%	ppm	ppm	ppm	ppm	wt%	wt%
BO 133-01/S2	b.d.l.	0.77	8.85	8.81	107	52	2.16	9.15	b.d.l.	115	b.d.l.	0.04	0.01	761	18	73	b.d.l.	70.10	100.00
BO 152-01/S2	3.72	6.53	39.52	4.57	888	167	0.20	18.88	219	47	0.70	6.99	16.44	160	285	67	267	2.23	99.99
BO 991/10/S1	b.d.l.	1.07	6.98	10.70	219	88	0.18	4.99	289	61	1.17	64.00	0.06	345	3491	107	35	10.38	100.00
BO 991/11/S1	b.d.l.	0.72	9.42	9.86	162	135	0.84	9.21	272	39	2.51	51.05	0.23	1303	2748	146	39	15.67	100.00
BO 991/13/S1	b.d.l.	b.d.l.	b.d.l.	10.58	62	b.d.l.	b.d.l.	0.36	21	119	0.17	4.49	0.01	3603	195	1230	8	83.84	99.98
BO 991/2/S1	b.d.l.	0.65	5.04	10.32	218	b.d.l.	0.11	6.62	237	62	3.88	44.52	0.17	1367	2096	313	38	28.26	100.00
BO 991/3/S1	b.d.l.	0.45	8.61	11.41	193	156	0.50	8.18	385	92	3.67	63.55	0.29	438	3707	75	79	2.81	100.00
BO N03/S2	0.75	0.73	4.33	3.78	357	379	11.84	41.13	b.d.l.	20	0.07	5.44	0.01	341	333	119	32	31.76	100.00
Average	**0.6**	**1.4**	**10.3**	**8.8**	**276**	**122**	**2.0**	**12.3**	**178**	**69**	**1.5**	**30.0**	**2.2**	**1040**	**1609**	**266**	**62**	**30.6**	**100.0**
Minimum	b.d.l.	b.d.l.	b.d.l.	3.78	62	b.d.l.	b.d.l.	0.36	b.d.l.	20	b.d.l.	0.04	0.01	160	17	67	b.d.l.	2.23	
Maximum	3.72	6.53	39.52	11.41	888	379	11.84	41.13	385	119	3.88	64.00	16.44	3603	3707	1230	267	83.84	
Standard deviation	1.30	2.11	12.19	2.93	262	123	4.05	12.76	150	36	1.61	28.33	5.78	1129	1576	398	86	30.73	
Coefficient of variation (%)	233	155	118	33	95	100	204	104	84	52	106	94	268	109	98	149	138	100	

Table A4.2. *Measurements of the chemical composition of pieces of ore from the Bockhart mine. Each measured value is the results of three consecutive runs using the "Alloy" method. The detected values for cobalt reflect some contamination from the preparation process of the pressed pellets (b.d.l.: below detection limit).*

A4.3. Ore specimens from the Erzwies mining site

	Mg	Al	Si	S	Ti	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Ag	Cd	Sb	Ba	Pb	Total
	wt%	wt%	wt%	wt%	ppm	ppm	wt%	wt%	ppm	ppm	ppm	wt%	ppm	ppm	ppm	ppm	ppm	wt%	wt%
ER S001/S2	1.63	0.31	0.60	0.63	32	390	25.02	71.71	b.d.l.	12	35	b.d.l.	244	b.d.l.	b.d.l.	b.d.l.	13	0.03	100.00
ER S002/S2	b.d.l.	1.34	16.37	6.73	134	101	2.63	11.02	b.d.l.	166	b.d.l.	0.08	128	589	23	61	14	61.71	100.00
ER S003/S2	b.d.l.	0.73	4.46	7.58	282	123	0.89	5.46	332	178	3293	79.61	b.d.l.	45	5582	73	19	0.27	100.00
ER S004/S2	0.44	1.04	9.65	4.58	332	382	12.09	34.48	b.d.l.	49	190	10.01	b.d.l.	378	742	110	48	27.48	100.00
ER S005/S2	b.d.l.	b.d.l.	1.52	10.16	182	140	1.59	8.78	301	47	670	55.43	b.d.l.	294	3200	104	b.d.l.	22.02	100.00
Average	**0.4**	**0.7**	**6.5**	**5.9**	**192**	**227**	**8.4**	**26.3**	**127**	**90**	**838**	**29.0**	**74**	**261**	**1910**	**70**	**19**	**22.3**	**100.0**
Minimum	b.d.l.	b.d.l.	0.60	0.63	32	101	0.89	5.46	b.d.l.	12	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	0.03	
Maximum	1.63	1.34	16.37	10.16	332	390	25.02	71.71	332	178	3293	79.62	244	589	5582	110	48	61.71	
Standard deviation	0.70	0.54	6.54	3.58	119	146	10.32	27.86	174	76	1399	36.40	110	244	2435	44	18	25.31	
Coefficient of variation (%)	170	79	100	60	62	64	122	106	137	84	167	125	148	93	128	63	93	113	

Table A4.3. *Measurements of the chemical composition of pieces of ore from the Erzwies mining site. Each measured value is the results of three consecutive runs using the "Alloy" method. The detected values for cobalt reflect some contamination from the preparation process of the pressed pellets (b.d.l.: below detection limit).*

A4.4. Slag specimens from the Angertal smelting site

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	FeO	CuO	ZnO	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
AN 113-01/S2	b.d.l.	1.33	4.83	29.25	b.d.l.	1.48	1.35	3.41	0.19	4.11	33.62	0.40	4.12	15.55
AN 113-03/S2	b.d.l.	1.37	4.43	28.91	0.02	5.38	1.24	2.18	0.16	6.35	39.40	0.37	5.72	4.33
AN 113-04/S2	b.d.l.	1.43	4.69	26.29	0.07	2.82	1.26	2.52	0.16	8.11	43.57	0.52	3.14	5.19
AN 117-01/S2	b.d.l.	0.05	1.66	16.19	b.d.l.	16.95	0.51	0.57	0.06	2.45	49.62	1.05	7.39	3.37
AN 117-02/S2	b.d.l.	0.03	1.55	15.68	b.d.l.	16.38	0.50	0.56	0.06	2.44	48.71	1.48	7.36	5.06
AN 130-01/S2	b.d.l.	0.19	1.73	15.20	b.d.l.	17.00	0.49	0.54	0.07	2.23	45.64	1.88	6.64	8.17
AN 130-10/S2	b.d.l.	1.48	4.80	24.84	0.08	3.84	1.12	2.66	0.17	11.26	40.37	0.25	4.01	4.97
AN 134a-01/S2	b.d.l.	1.28	5.88	28.15	0.11	3.95	1.40	2.90	0.21	7.54	40.39	0.37	3.76	3.86
AN 134a-02/S2	1.00	1.05	4.20	26.00	0.02	2.72	1.11	2.43	0.17	7.90	42.76	0.41	1.29	8.63
AN 134a-02/S2	1.21	1.46	4.26	25.66	b.d.l.	2.72	1.09	2.42	0.16	7.64	41.76	0.40	1.25	9.48
AN 134b-01/S2	b.d.l.	0.22	1.68	16.76	b.d.l.	15.16	0.54	0.58	0.06	2.61	51.21	0.81	7.35	2.91
AN 148-01/S2	b.d.l.	0.57	3.15	20.94	0.01	8.36	0.83	1.04	0.10	2.54	55.96	1.16	2.31	2.89
AN 170-03/S2	1.23	0.60	4.81	30.93	0.03	5.38	1.14	1.11	0.14	1.41	50.38	0.43	1.35	0.92
AN 187-02/S2	0.68	0.76	4.50	34.69	0.04	5.60	1.01	1.52	0.15	2.13	47.61	0.14	0.75	0.31
Average	**0.3**	**0.8**	**3.7**	**24.3**	**0.03**	**7.7**	**1.0**	**1.8**	**0.1**	**4.9**	**45.1**	**0.7**	**4.0**	**5.4**
Minimum	b.d.l.	0.03	1.55	15.20	b.d.l.	1.48	0.49	0.54	0.06	1.41	33.62	0.14	0.75	0.31
Maximum	1.23	1.48	5.88	34.69	0.11	17.00	1.40	3.41	0.21	11.26	55.96	1.88	7.39	15.55
Standard deviation	0.50	0.56	1.47	6.28	0.04	5.95	0.33	1.01	0.05	3.12	5.89	0.51	2.48	3.96
Coefficient of variation (%)	169	67	40	26	133	77	34	58	39	64	13	75	62	73

Table A4.4a. *Measurements of the chemical composition of pieces of slag from the Angertal. Each measured value is the results of three consecutive runs using the "Turboquant" (Tq-0261a) method. The detected values for cobalt reflect some contamination from the preparation process of the pressed pellets (b.d.l.: below detection limit).*

A4.4 Slag specimens from the Angertal smelting site (continued)

	V_2O_5	Cr_2O_3	Co_3O_4	NiO	As_2O_3	SrO	ZrO_2	Ag	CdO	Sb	Ba	Hg	Tl	Total
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	wt%
AN 113-01/S2	29	b.d.l.	215	68	1102	372	75	6	2	569	464	57	262	100.00
AN 113-03/S2	58	64	b.d.l.	40	312	218	45	39	11	105	366	18	71	99.99
AN 113-04/S2	70	27	b.d.l.	58	1083	236	44	15	3	125	336	27	72	99.99
AN 117-01/S2	23	b.d.l.	295	b.d.l.	171	82	21	161	61	100	173	4	14	100.00
AN 117-02/S2	48	12	314	19	200	91	28	233	448	136	163	5	54	100.00
AN 130-01/S2	25	b.d.l.	413	b.d.l.	321	117	14	326	539	161	167	26	126	100.00
AN 130-10/S2	97	130	b.d.l.	102	326	213	33	32	2	57	270	26	59	100.00
AN 134a-01/S2	109	82	b.d.l.	12	722	302	75	22	6	79	442	22	44	99.99
AN 134a-02/S2	109	138	b.d.l.	29	1320	290	58	17	2	181	278	26	183	99.99
AN 134a-02/S2	65	98	b.d.l.	43	2937	300	63	36	b.d.l.	219	292	22	168	100.00
AN 134b-01/S2	b.d.l.	b.d.l.	321	b.d.l.	178	78	36	139	25	94	175	3	23	100.00
AN 148-01/S2	41	38	406	b.d.l.	142	131	29	79	b.d.l.	81	335	b.d.l.	25	100.00
AN 170-03/S2	56	b.d.l.	460	b.d.l.	326	109	48	24	b.d.l.	24	252	21	b.d.l.	100.00
AN 187-02/S2	98	16	322	b.d.l.	185	104	41	31	b.d.l.	8	220	b.d.l.	b.d.l.	100.00
Average	**59**	**43**	**196**	**26**	**666**	**189**	**44**	**83**	**79**	**139**	**281**	**18**	**79**	**100.0**
Minimum	b.d.l.	b.d.l.	b.d.l.	b.d.l.	142	78	14	6	b.d.l.	8	163	b.d.l.	b.d.l.	
Maximum	109	138	460	102	2937	372	75	326	539	569	464	57	262	
Standard deviation	34	50	185	32	766	99	19	97	178	136	99	15	78	
Coefficient of variation (%)	58	116	95	121	115	53	43	117	226	99	35	84	99	

Table A4.4b. *Measurements of the chemical composition of pieces of slag from the Angertal. Each measured value is the results of three consecutive runs using the "Turboquant" (Tq-0261a) method. The detected values for cobalt reflect some contamination from the preparation process of the pressed pellets (b.d.l.: below detection limit).*

A4.5. Matte specimens from the Angertal smelting site

	Mg	Al	Si	S	Mn	Fe	Cu	Zn	As	Ag	Pb
	wt%	wt%	wt%	wt%	wt%	wt%	ppm	wt%	wt%	ppm	wt%
AN 15-01/S2	b.d.l.	b.d.l.	0.33	13.29	0.69	74.04	3.44	3.39	0.27	0.21	4.17
AN 81-01/S1	0.35	3.81	18.66	3.69	2.56	56.24	0.42	11.35	0.08	0.04	2.51
AN 81-02/S2	1.20	7.96	28.10	4.60	0.10	15.47	3.35	1.61	1.77	0.21	34.61
AN 88-01/S2	b.d.l.	b.d.l.	b.d.l.	10.50	0.05	51.66	20.49	0.19	0.11	0.66	16.06
AN 104-01/S2	b.d.l.	0.02	1.53	11.14	0.33	36.78	18.21	2.90	0.19	0.50	28.20
AN 108-04/S1	b.d.l.	b.d.l.	b.d.l.	13.41	0.22	40.42	24.94	2.22	0.36	0.50	17.64
AN 108-05/S1	b.d.l.	b.d.l.	b.d.l.	12.31	0.23	46.07	22.93	2.33	0.29	0.41	15.18
AN 108-07/S1	b.d.l.	b.d.l.	b.d.l.	11.85	0.25	47.02	20.42	2.73	0.34	0.44	16.70
Average	**0.2**	**1.5**	**6.1**	**10.1**	**0.6**	**46.0**	**14.3**	**3.3**	**0.4**	**0.4**	**16.9**
Minimum	b.d.l.	b.d.l.	b.d.l.	3.69	0.05	15.47	0.42	0.19	0.08	0.04	2.51
Maximum	1.20	7.96	28.10	13.41	2.56	74.04	24.94	11.35	1.77	0.66	34.61
Standard deviation	0.42	2.94	10.99	3.81	0.83	16.78	10.07	3.38	0.55	0.20	10.79
Coefficient of variation (%)	219	199	181	38	150	37	71	101	129	55	64

Table A4.5a. *Measurements of the chemical composition of pieces of matte from the Angertal smelting site. Each measured value is the results of three consecutive runs using the "Alloy" method. The detected values for cobalt reflect some contamination from the preparation process of the pressed pellets (b.d.l.: below detection limit).*

A4.5. Matte specimens from the Angertal smelting site (continued)

	P	Ti	Cr	Co	Ni	Zr	Cd	Sb	Ba	Total
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	wt%
AN 15-01/S2	b.d.l.	198	359	868	b.d.l.	12	17	191	5	100.00
AN 81-01/S1	53	1387	385	369	b.d.l.	73	7	51	726	100.00
AN 81-02/S2	b.d.l.	4948	231	242	129	104	244	244	2570	99.85
AN 88-01/S2	b.d.l.	107	334	900	1326	b.d.l.	3	113	17	100.00
AN 104-01/S2	b.d.l.	257	255	614	117	b.d.l.	11	737	b.d.l.	100.00
AN 108-04/S1	b.d.l.	196	305	1075	0303	b.d.l.	10	883	b.d.l.	100.00
AN 108-05/S1	b.d.l.	139	305	948	356	4	8	699	b.d.l.	100.00
AN 108-07/S1	b.d.l.	138	335	810	488	b.d.l.	6	743	b.d.l.	100.00
Average	**7**	**921**	**314**	**728**	**340**	**24**	**38**	**458**	**415**	**100.0**
Minimum	b.d.l.	107	231	242	b.d.l.	b.d.l.	3	51	b.d.l.	
Maximum	53	4948	385	1075	1326	104	244	883	2570	
Standard deviation	19	1682	51	293	435	41	83	338	907	
Coefficient of variation (%)	283	183	16	40	128	169	217	74	219	

Table A4.5b. *Measurements of the chemical composition of pieces of matte from the Angertal smelting site. Each measured value is the results of three consecutive runs using the "Alloy" method. The detected values for cobalt reflect some contamination from the preparation process of the pressed pellets (b.d.l.: below detection limit).*

Appendix 5 – Chemical composition by SEM-EDS area analysis[10], normalised to 100%, of cross-sections of cupels used in the experimental cupellation

A5. 1 Cupel specimen AN 196-01 Cup1/S2 (cupellation of lead)

	Na_2O	MgO	SiO_2	P_2O_5	CaO	As_2O_3	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	1.1	1.1	2.1	34.5	43.0	b.d.l.	18.3
Measure 2	1.1	1.0	1.6	32.1	40.6	b.d.l.	23.8
Measure 3	1.2	1.0	1.6	32.2	41.0	b.d.l.	23.1
Measure 4	1.1	b.d.l.	1.8	28.1	33.6	2.5	32.9
Mean	**1.1**	**0.8**	**1.8**	**31.7**	**39.5**	**0.6**	**24.5**
Minimum	1.1	b.d.l.	1.6	28.1	33.6	b.d.l.	18.3
Maximum	1.2	1.1	2.1	34.5	43.0	2.5	32.9
Standard deviation	0.1	0.5	0.2	2.6	4.1	1.2	6.1
Coefficient of variation (%)	7	68	14	8	10	200	25

Table A5.1. *Chemical composition of cupel specimen AN 196-01 Cup 1/S2 (b.d.l.: below detection limit).*

[10] Area of analysis of 1.2 mm by 0.9 mm, at magnification 100.

A5.2. Cupel specimen AN 108-04 Cup 2/S2 (cupellation of matte)

	Na_2O	MgO	SiO_2	P_2O_5	SO_3	CaO	FeO	CuO	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	1.47	0.82	1.16	36.98	8.67	47.20	b.d.l.	b.d.l.	3.69
Measure 2	1.40	0.88	1.24	32.90	7.76	41.88	1.79	1.01	11.15
Measure 3	1.22	0.83	1.00	30.29	6.58	37.50	2.66	1.61	18.42
Measure 4	1.68	0.85	1.00	30.03	6.42	37.89	3.69	1.17	17.27
Measure 5	1.94	0.83	1.33	32.96	6.26	39.72	2.11	1.41	13.45
Measure 6	2.58	0.85	1.09	32.35	5.93	40.60	1.78	1.10	13.73
Measure 7	2.18	0.97	1.19	32.17	4.81	40.10	2.14	1.64	14.79
Measure 8	1.58	0.81	4.46	32.37	4.61	40.33	b.d.l.	0.77	15.17
Measure 9	0.99	0.86	1.05	28.43	b.d.l.	37.07	0.93	2.31	28.36
Measure 10	1.15	0.64	0.89	31.14	2.04	37.60	3.96	2.64	19.94
Measure 11	1.40	0.59	1.02	26.91	b.d.l.	32.94	12.07	1.54	23.54
Measure 12	1.92	0.45	0.96	25.45	1.88	30.27	17.46	1.79	19.82
Mean	**1.6**	**0.8**	**1.4**	**31.0**	**4.6**	**38.6**	**4.0**	**1.4**	**16.6**
Minimum	1.0	0.5	0.9	25.5	b.d.l.	30.3	b.d.l.	b.d.l.	3.7
Maximum	2.6	1.0	4.5	37.0	8.7	47.2	17.5	2.6	28.4
Standard deviation	0.5	0.1	1.0	3.1	2.9	4.3	5.3	0.7	6.3
Coefficient of variation (%)	28	19	72	10	64	11	130	49	38

Table A5.2. *Chemical composition of cupel specimen AN 108-04 Cup 2/S2 (b.d.l.: below detection limit).*

A5.3. Cupel specimen AN 88-03 Cup/S1 (cupellation of matte)

	Na_2O	MgO	SiO_2	P_2O_5	SO_3	CaO	FeO	CuO	PbO
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
Measure 1	1.41	0.86	1.31	33.82	6.64	39.72	1.57	1.26	13.42
Measure 2	1.04	0.94	0.97	27.41	10.45	33.80	7.08	0.89	17.42
Measure 3	0.85	0.95	2.37	40.53	1.25	48.77	b.d.l.	b.d.l.	4.97
Measure 4	4.04	1.33	1.30	40.45	3.66	48.88	b.d.l.	b.d.l.	b.d.l.
Measure 5	1.09	0.90	1.20	33.13	7.94	38.93	1.54	0.91	14.35
Measure 6	1.45	1.06	1.61	37.09	8.24	46.91	b.d.l.	b.d.l.	3.65
Measure 7	1.61	0.64	b.d.l.	31.25	1.98	38.03	5.58	5.82	15.08
Measure 8	0.58	1.04	b.d.l.	34.33	8.41	40.23	b.d.l.	b.d.l.	15.41
Measure 9	1.23	0.58	1.28	29.04	3.35	34.51	13.10	2.19	14.72
Mean	**1.5**	**0.9**	**1.1**	**34.1**	**5.8**	**41.1**	**3.2**	**1.2**	**11.0**
Minimum	0.6	0.6	b.d.l.	27.4	1.3	33.8	b.d.l.	b.d.l.	b.d.l.
Maximum	4.0	1.3	2.4	40.5	10.5	48.9	13.1	5.8	17.4
Standard deviation	1.0	0.2	0.7	4.6	3.3	5.8	4.5	1.9	6.3
Coefficient of variation (%)	68	24	67	14	57	14	142	153	57

Table A5.3. *Chemical composition of cupel specimen AN 88-03 Cup/S1 (b.d.l.: below detection limit).*

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